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QUALITY ASSURANCE PROJECT PLAN (QAPjP)
REMEDIAL INVESTIGATION/FEASIBILITY STUDY

H.O.D. LANDFILL
ANTIOCH, ILLINOIS

VOLUME 1 of 2

DECEMBER 1992

PREPARED FOR:
WASTE MANAGEMENT OF ILLINOIS, INC.
WESTCHESTER, ILLINOIS

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QUALITY ASSURANCE PROJECT PLAN (QAPjP)
REMEDIAL INVESTIGATION/FEASIBILITY STUDY
H.O.D LANDFILL
ANTIOCH, ILLINOIS
(December 1992)

Prepared By:

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U.S. EPA, Region V, Quality Assurance Manager

QUALITY ASSURANCE PROJECT PLAN (QAPjP)
REMEDIAL INVESTIGATION/FEASIBILITY STUDY
H.O.D. LANDFILL SITE
ANTIOCH, ILLINOIS

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LIST OF ACRONYMS AND ABBREVIATIONS

AOC	Administrative Order on Consent
ARAR	Applicable or Relevant and Appropriate Requirements
ASTM	American Standards for Testing Materials
CDO	Central District Office
CLP	Contract Laboratory Program
CRDL	Contract Required Detection Limits
CRQL	Contract Required Quantitation Limits
CRL	Central Regional Laboratory
DQO	Data Quality Objective
ESI	Expanded Site Inspection
ETC	Environmental Testing and Certification Corporation
FIT	Field Investigation Team
HRS	Hazard Ranking System
HSP	Site Specific Health and Safety Plan
IEPA	Illinois Environmental Protection Agency
LL TAL	Low Level Detection Target Analyte List
LL TCL	Low Level Detection Target Compound List
MS/MSD	Matrix Spike/Matrix Spike Duplicate
NPL	National Priorities List
PA	Preliminary Assessment
PRP	Potentially Responsible Party
QA	Quality Assurance
QAO	Quality Assurance Officer
QAPjP	Quality Assurance Project Plan
QAS	Quality Assurance Section
QC	Quality Control
RI/FS	Remedial Investigation/Feasibility Study
RMAL	Rocky Mountain Analytical Laboratory
RPD	Relative Percent Difference
RPM	Remedial Project Manager
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure
SOW	Statement of Work
TAL	Target Analyte List
TDS	Total Dissolved Solids
TCL	Target Compound List
TIC	Tentatively Identified Compound
TOC	Total Organic Carbon
U.S. EPA	United States Environmental Protection Agency, Region V
VOA	Volatile Organic Analysis
Warzyn	Warzyn Inc.
WMII	Waste Management of Illinois, Inc.

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INTRODUCTION

The United States Environmental Protection Agency (U.S. EPA) requires that all environmental monitoring and measurement efforts mandated or supported by U.S EPA participate in a centrally managed quality assurance (QA) program.

Any party generating data under this program has the responsibility to implement minimum procedures to assure that precision, accuracy, completeness, and representativeness of its data are known and documented. To ensure the responsibility is met uniformly, each party must prepare a written QA Project Plan (QAPjP) covering each project it is to perform.

This QAPjP presents the organization, objectives, functional activities, and specific Quality Assurance (QA) and Quality Control (QC) activities associated with the Remedial Investigation/Feasibility Study (RI/FS) for the H.O.D. Landfill Site. This QAPjP also describes the specific protocols which will be followed for sampling, sample handling and storage, chain of custody, and laboratory and field analysis.

All QA/QC procedures will be in accordance with applicable professional technical standards, U.S. EPA requirements, government regulations and guidelines, and specific project goals and requirements. This QAPjP is prepared by Warzyn Inc. (Warzyn) in accordance with the U.S. EPA QAPjP guidance documents:

- U.S. EPA, December 1980, Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans, QAMS-005/80
- U.S. EPA, May 1991, Region V Model Superfund Quality Assurance Project Plan
- U.S. EPA, January 1989, Region V Content Requirements for Quality Assurance Project Plan

SECTION 1

PROJECT DESCRIPTION

1.1 Site History and Background Information

The H.O.D. Landfill Site (Site) is an inactive landfill located in the eastern boundary of the Village of Antioch in Lake County in northeastern Illinois (Township 46 North, Range 10 East, Sections 8 and 9). The Site is bordered on the south and west by Sequoit Creek. The Silver Lake residential subdivision is located east of the Site, and agricultural land, scattered residential areas, and undeveloped land is located to the north. A large wetland area extends south of the Site from Sequoit Creek. Silver Lake is located approximately 200 feet southeast of the Site. A large industrial park area (Sequoit Acres Industrial Park), constructed on former landfill and fill areas, is located west of the Site and borders Sequoit Creek. Refer to Figure 1-1 for the Site Location Map.

The Site consists of a total of 80 acres, of which 51 acres which have been landfilled. Although the landfilled area is visually continuous, it consisted of two separate landfill areas, identified as the "old" and "new" landfills. The "old" landfill, consisting of 24.2 acres situated on the western third of the property, operated between 1963 and 1975. The "new" landfill, consisting of 26.8 acres situated immediately east of the "old" landfill, operated between 1975 and 1984. The landfill accepted both municipal waste and a variety of industrial and special wastes.

A more detailed description of the site history and background are contained in the Work Plan.

1.2 Past Data Collection Activity / Current Status

The Site has been subject to a number of investigations since 1973. A discussion of the investigations is provided in Section 3.1.6 of the Work Plan.

A Preliminary Assessment (PA) was prepared by the E&E Field Investigation Team (FIT) for U.S. EPA in 1983. The FIT conducted a site inspection on July 10, 1984; the Site was given a Hazard Ranking System (HRS) model score of 52.02. At that time, the U.S. EPA proposed the Site be placed on the National Priorities List (NPL).

An Expanded Site Inspection (ESI) was conducted by E&E during the period of 1986 through 1989, resulting in an ESI report submitted to U.S. EPA on September 22 , 1989. In January 1990, the H.O.D. Landfill was rescored under the HRS and received a revised score of 34.68.

The Site was placed on the NPL in February 1990. On August 20, 1990 Waste Management of Illinois, Inc. (WMII) and U.S. EPA entered an Administrative Order on Consent (AOC) to conduct a Potentially Responsible Party (PRP) lead RI/FS at the Site. Warzyn was contracted by WMII to support the PRP lead RI/FS effort in developing the RI/FS Work Plan and other planning documents, including this QAPjP.

1.3 Project Objectives and Scope

The purpose of the RI is to gather sufficient information to quantify risk to public health and environment (Baseline Risk Assessment) and to develop and evaluate viable remedial alternatives (Feasibility Study) at the Site. The objectives of the RI are to determine the nature and extent of contamination at the Site in order to support the activities of the FS. The objective of the RI/FS is to develop and evaluate appropriate remedial action alternatives based on the RI/FS data.

The objectives of the data collection are as follows:

- Further define the nature and extent of contamination in previously identified on-site and off-site areas

- Determine the nature and extent of contamination in previously uninvestigated areas

- Collect sufficient data on all contaminated media to support the baseline risk assessment and feasibility study.

All tasks, subtasks and activities are directed toward the accomplishment of these primary objectives. Refer to the Work Plan Section 4.4.3 for a detailed description of the RI tasks, subtasks and activities.

1.4 Sample Network Design and Rationale

The sample network design and rationale for sample locations is described in detail in Section 3 of the Sampling and Analysis Plan (SAP) (refer to Appendix A).

1.5 Parameters to be Tested and Frequency

Sample matrices, analytical parameters, and frequencies of sample collection can be found in Table 1-1. A summary of sample volume, bottle, preservative, and packaging requirements is provided in Table 1-2.

1.6 Intended Data Usage and Data Quality Objectives

Data Quality Objectives (DQOs) are qualitative and quantitative statements which specify the quality of the data required to support decisions made during the RI/FS activities, and are based on the end uses of the data to be collected. As such, different data uses may require different levels of data quality. There are five analytical levels which address various data uses and the QA/QC effort and methods required to achieve the desired level of quality. These levels are:

- Screening (DQO Level I): This provides the lowest data quality but the most rapid results. It is often used for health and safety monitoring at the Site, preliminary comparison to Applicable or Relevant and Appropriate Requirements (ARARs),

Target Compound List (TCL) organic and Target Analyte List (TAL) inorganic parameters for groundwater, sediment/soil, leachate, and surface water matrices. Low level TCL organic and low level TAL inorganic data for municipal/private wells will also fall under DQO Level IV.

- Non-Standard (DQO Level V): This refers to analyses by non-standard protocols, for example, when exacting detection limits or analysis of an unusual chemical compound is required. These analyses often require method development or adaptation. The level of quality control is usually similar to DQO Level IV data. For the H.O.D. Landfill Site, data generated under DQO Level V are the volatiles for the landfill gas samples and indicator parameters (alkalinity, chloride, hardness, sulfate, total organic carbon (TOC), total dissolved solids (TDS), nitrate nitrogen, nitrite nitrogen, and ammonia nitrogen) for groundwater and leachate.

A summary of data generating activities, intended data uses and associated DQOs for the H.O.D. Landfill Site are presented in Table 1-3.

1.7 Project Schedule

A schedule of RI/FS activities for the H.O.D. Landfill Site is summarized in Figure 1-2.

Target Compound List (TCL) organic and Target Analyte List (TAL) inorganic parameters for groundwater, sediment/soil, leachate, and surface water matrices. Low level TCL organic and low level TAL inorganic data for municipal/private wells will also fall under DQO Level IV.

- Non-Standard (DQO Level V): This refers to analyses by non-standard protocols, for example, when exacting detection limits or analysis of an unusual chemical compound is required. These analyses often require method development or adaptation. The level of quality control is usually similar to DQO Level IV data. For the H.O.D. Landfill Site, data generated under DQO Level V are the volatiles for the landfill gas samples and indicator parameters (alkalinity, chloride, hardness, sulfate, total organic carbon (TOC), total dissolved solids (TDS), nitrate nitrogen, nitrite nitrogen, and ammonia nitrogen) for groundwater and leachate.

A summary of data generating activities, intended data uses and associated DQOs for the H.O.D. Landfill Site are presented in Table 1-3.

1.7 Project Schedule

A schedule of RI/FS activities for the H.O.D. Landfill Site is summarized in Figure 1-2.

SECTION 2

PROJECT ORGANIZATION AND RESPONSIBILITY

Warzyn will be conducting all phases of the RI/FS. Warzyn will perform the field investigation, prepare the RI report, and perform the subsequent feasibility study. Project management will also be provided by Warzyn, under the direction of WMII. The various quality assurance and management responsibilities of key project personnel are defined below. Refer to Figure 2-1 for the project organizational chart.

2.1 Overall Responsibility

U.S. EPA Remedial Project Manager

The U.S. EPA Remedial Project Manager (RPM) is Fred Micke. The RPM has the overall responsibility for all phases of the RI/FS.

IEPA State Project Manager

The IEPA State Project Manager is Charlene Falco. The IEPA State Project Manager will be involved in the project as agreed between U.S. EPA and IEPA.

WMII Site Project Manager

The Site Project Manager is March Smith. The Site Project Manager is responsible for implementing the project, and has the authority to commit the resources necessary to meet project objectives and requirements. The Site Project Manager's primary function is to ensure that technical, financial, and scheduling objectives are achieved successfully and will provide the major point of contact and control for matters concerning the project.

Warzyn Project Manager

The Warzyn Project Manager is Gary Parker. The Warzyn Project Manager has the overall responsibility for ensuring that the project meets U.S. EPA objectives and Warzyn's quality standards. In addition, he is responsible for technical quality control and project oversight, and will provide the Site Project Manager with access to corporate management.

The WMII Site Project Manager and Warzyn Project Manager will:

- Define project objectives and develop a detailed work plan schedule
- Establish project policy and procedures to address the specific needs of the project as a whole, as well as the objectives of each task
- Acquire and apply technical and corporate resources as needed to ensure performance within budget and schedule constraints
- Orient all field leaders and support staff concerning the project's special considerations
- Monitor and direct the field leaders
- Develop and meet ongoing project and/or task staffing requirements, including mechanisms to review and evaluate each task product
- Review the work performed on each task to ensure its quality, responsiveness, and timeliness
- Review and analyze overall task performance with respect to planned requirements and authorizations
- Approve all external reports (deliverables) before their submission to U.S. EPA
- Ultimately be responsible for the preparation and quality of interim and final reports
- Represent the project team at meetings and public hearings

Warzyn Remedial Investigation Leader

The Warzyn RI Leader is Al Schmidt. The RI Leader is a support to the Warzyn Project Manager. He is responsible for leading and coordinating the day-to-day activities of the various resource specialists under his supervision. The RI Leader is a highly experienced environmental professional and will report directly to the Warzyn Project Manager. Specific responsibilities include:

- Provision of day-to-day coordination with the Project Managers on technical issues in specific areas of expertise
- Development and implementation of field-related work plans, assurance of schedule compliance, and adherence to management-developed study requirements
- Coordination and management of field staff including sampling, drilling, and other investigative work
- Implementation of QC for technical data provided by the field staff including field measurement data
- Adherence to established project schedule
- Review and approval of text and graphics required for field team efforts
- Coordination and oversight of technical efforts of subcontractors assisting the field team
- Identification of problems at the field team level, discussion of resolutions with the Project Managers, and provision of communication between team and upper management
- Participation in the preparation of the final RI report

Technical Staff

The technical staff for this project will be drawn from Warzyn's pool of company resources. The technical team staff will be utilized to gather and analyze data, and to prepare various task reports and support materials. All of the designated technical team staff are experienced professionals

who possess the degree of specialization and technical competence required to effectively and efficiently perform the required work.

Warzyn Quality Assurance Officer

The Warzyn Quality Assurance Officer (QAO) is Kevin Domack. The QAO will remain independent of direct job involvement and day-to-day operations, and has direct access to corporate executive staff as necessary to resolve any QA dispute. He is responsible for auditing the implementation of the QA program in conformance with the demands of specific investigations, Warzyn's policies, and U.S. EPA requirements. Specific functions and duties include:

- Provide QA audit on various phases of the field operations
- Review and approval of QA plans and procedures
- Provide QA technical assistance to project staff

U.S. EPA Quality Assurance Manager

The U.S. EPA QAM has the responsibility to review and approve the QAPjP. The U.S. EPA QAO is Valerie Jones.

2.2 Specialized Responsibilities

2.2.1 Monitoring and Sampling Operations and QC

- Principal Engineering Firm - Warzyn, Chicago, Illinois
- Drilling - To be determined through bidding process
- Sampling, Monitoring and Survey - Warzyn, Chicago, Illinois
- On Site Day-to-day Field Activities - RI Leader, Warzyn, Chicago, Illinois

- Quality Control - QAO, Warzyn, Chicago, Illinois

2.2.2 Laboratory Analysis

- Analysis of groundwater, surface water, sediment/soil, and leachate samples for TCL organics and TAL inorganics as specified in Table 1-1:

  Environmental Testing and Certification Corporation (ETC)
  284 Raritan Center Parkway
  Edison, New Jersey 08818

- Analysis of sediment/soil for TOC as specified in Table 1-1:

  ETC
  284 Raritan Center Parkway
  Edison, New Jersey 08818

- Analysis of groundwater and leachate for indicator parameters (alkalinity, chloride, hardness, sulfate, TOC, TDS, nitrate nitrogen, nitrite nitrogen, and ammonia nitrogen) as specified in Table 1-1:

  Warzyn Analytical Laboratory
  One Science Court
  Madison, WI 53711

- Analysis of municipal/private well samples for low level TCL organics as specified in

Table 1-1:

CompuChem Laboratories
3308 Chapel Hill/Nelson Highway
Research Triangle Park, NC 27709

- Analysis of municipal/private well samples for low level TAL inorganics as specified in Table 1-1:

Warzyn Analytical Laboratory
One Science Court
Madison, WI 53711

- Analysis of landfill gas samples for volatile organics as specified in Table 1-1:

Enseco - Air Toxics Laboratory
9537 Telstar Avenue, Suite 118
El Monte, California 91731

- Analysis of sediment/soil samples for physical characteristics (grain size, natural moisture content, atterberg limits, permeability, and density) as specified in Table 1-1:

Warzyn Soils Laboratory
505 Science Drive, Suite C
Madison, Wisconsin 53711

- Analysis of soil samples for clay mineralogy using x-ray diffraction as specified in

Table 1-1:

Core Laboratories Inc.
1875 Monetary Lane
Carrollton, Texas 75006

2.2.3 Laboratory Data and QC

Laboratory Data

- Analytical protocol specified - Warzyn, Chicago, Illinois
- Review of analytical protocol - ETC, Edison, New Jersey
- Review of analytical procedures - U.S. EPA Region V Quality Assurance Section (QAS) and Central Regional Laboratory (CRL), Chicago, Illinois
- Internal QA/QC - Laboratory QAO, ETC, Edison, New Jersey
- Final data review and validation - Chemist, Warzyn, Chicago, Illinois
- Review of tentatively identified compounds and assessment of need for confirmation - Chemist, Warzyn, Chicago, Illinois

2.2.4 Performance and Systems Audits

Field Operations

- Internal Audits - QAO, Warzyn, Chicago, Illinois
- External Audits - U.S. EPA Region V CRL and Central District Office (CDO), Chicago, Illinois

Analytical Laboratories

- Internal Audits - Laboratory QAO, ETC, Edison, New Jersey

- External Audits - U.S. EPA Region V CRL, Chicago, Illinois

Final Evidence File

- Final Evidence File Audits - QAO, Warzyn, Chicago, Illinois

SECTION 3

QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

The overall QA objective is to develop and implement procedures for field sampling, chain-of-custody, laboratory analysis, and reporting that will provide results which are legally defensible in a court of law. Specific procedures for sampling, chain-of-custody, laboratory instruments calibration, laboratory analysis, reporting of data, internal quality control, audits, preventive maintenance of field equipment, and corrective action are described in other sections of this QAPjP. The purpose of this section is to address the specific objectives for accuracy, precision, completeness, representativeness, and comparability.

3.1 Level of Quality Control Effort

Field blank, trip blank, duplicate, and matrix spike samples will be analyzed to assess the quality of the data resulting from the field sampling program. Field and trip blanks consisting of deionized water, will be submitted to the analytical laboratories to provide the means to assess the quality of the data resulting from the field sampling program. Field blank samples are analyzed to check for procedural contamination at the Site which may cause sample contamination. Trip blanks are used to assess the potential for contamination of samples due to contaminant migration during sample shipment and storage. Duplicate samples are analyzed to check for sampling and analytical reproducibility. Matrix spikes provide information about the effect of the sample matrix on the digestion and measurement methodology. Matrix spikes are performed in duplicate for organic analyses, and are hereinafter referred to as matrix spike/matrix spike duplicate (MS/MSD) samples. MS/MSD samples are designated/collected for organic analyses only.

The general level of the QC effort will be one field duplicate and one field blank for every 10 or fewer investigative samples. One volatile organic analysis (VOA) trip blank consisting of deionized, ultra pure water, will be included along with each shipment of aqueous VOA samples.

MS/MSD samples are not investigative samples; they are QC analyses performed on separate aliquots of investigative samples. Soil MS/MSD samples require no extra volume for VOAs or extractable organics. However, aqueous MS/MSD samples must be collected at triple the volume for VOAs and double the volume for extractable organics. One MS/MSD sample will be collected/designated for every 20 or fewer investigative samples per sample matrix (i.e., groundwater, soil). The number of field duplicate and field blank samples to be collected for this Site are listed in Table 1-1. Sampling procedures are specified in the SAP (refer to Appendix A).

Soil/sediment, landfill gas, groundwater, surface water, leachate, municipal well, and private well samples will be sent to ETC, CompuChem, Enseco - Air Toxics Laboratory, Warzyn, and Core for analysis. Parameter lists and required quantitation levels are summarized in Tables 3-1, 3-2, 3-3, 3-4, 3-5, and 3-6.

The level of laboratory QC effort for testing of TAL inorganics and TCL organics is specified in the current CLP Statements of Work (SOWs): ILM02.0 for inorganics (including low level inorganics), OLM01.8 for organics, and OLC01.0 for low level organics. The levels of laboratory QC effort for indicator parameters, field measurements, physical characteristics, and landfill gas volatiles are specified in Table 3-7.

3.2 Accuracy, Precision and Sensitivity of Analyses

The fundamental QA objective with respect to accuracy, precision, and sensitivity of laboratory analytical data is to achieve the QC acceptance criteria of the analytical protocols.

TCL Organics/TAL Inorganics

Laboratory analysis of TCL organics and TAL inorganics will follow the current CLP SOWs (OLM01.8 for organics, ILM02.0 for inorganics). The accuracy and precision, and sensitivity requirements are summarized within the CLP SOWs.

Low Level TCL Organics/TAL Inorganics

The laboratory analysis of low level TCL organics for private and municipal well samples will follow the current CLP SOW OLC01.0. The accuracy and precision, and sensitivity requirements for the low level TCL organics are summarized within the CLP SOW. The laboratory analysis of low level TAL inorganics for private and municipal well samples will follow the SOPs provided in Appendix B. The accuracy and precision requirements for the low level TAL inorganics are the same as those in the CLP SOW ILM02.0. The sensitivity requirements for these analyses are summarized in Table 3-4.

Indicators

SOPs for the indicator parameters (alkalinity, chloride, hardness, sulfate, TOC, TDS, nitrate nitrogen, nitrite nitrogen, and ammonia nitrogen) are provided in Appendix B. The accuracy and precision requirements for these analyses are summarized in Table 3-7. The sensitivity requirements for these analyses are summarized in Table 3-6.

Physical Characteristics

Physical characteristics of grain size, natural moisture content, atterberg limits, density, TOC, and clay mineralogy will follow the methods provided in Appendix B. The accuracy, precision, and sensitivity requirements for these analyses are summarized in Table 3-7.

Landfill Gas Volatiles

The SOP for the analysis of landfill gas for volatiles is provided in Appendix B. The accuracy and precision requirements are summarized in Table 3-7. The sensitivity requirements are summarized in Table 3-5.

Field Measurements

SOPs for the field equipment to measure pH, conductivity, temperature, dissolved oxygen, redox potential, methane, oxygen, carbon dioxide, Hnu screening of drill cuttings and are provided in Appendix C. The accuracy and precision requirements of these analyses are summarized in Table 3-7. The sensitivity requirements of these analyses are summarized in Table 3-6.

3.3 Completeness, Representativeness and Comparability

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. It is expected that the participating laboratories will provide data meeting QC acceptance criteria for 95 percent or more for all samples tested using the SOWs and SOPs referenced in Section 3.2. Following completion of the analytical testing, the percent completeness will be calculated by the following equation:

$$\text{Completeness } (\%) = A/B \times 100$$

where, A = number of valid data
B = number of samples collected for each parameter analyzed

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Representativeness is a qualitative parameter which is dependent upon the proper design of the sampling program and proper laboratory protocol. The sampling network was designed to provide data representative of Site conditions. During development of this network, consideration was given to past waste disposal practices, existing analytical data,

physical setting and processes, and constraints inherent to the Superfund program. The rationale of the sampling network is discussed in detail in the SAP. Representativeness will be satisfied by insuring that the SAP is followed, proper sampling technique are used, proper analytical procedure are followed, and holding times of the samples are not exceeded in the laboratory. Representativeness will be assessed by the analysis of field duplicate samples.

Comparability expresses the confidence with which one data set can be compared with another. The extent to which existing and planned analytical data will be comparable, depends on the similarity of sampling and analytical methods. The procedures used to obtain the planned analytical data, as documented in the QAPjP, are expected to provide comparable data. These new analytical data, however, may not be directly comparable to existing data because of differences in procedures and QA objectives.

SECTION 4
SAMPLING PROCEDURES

4.1 Sampling Procedures

Sampling procedures are described in the SAP which is contained in Appendix A of this document.

4.2 Bottle Requirements

The contaminant-free sample containers (bottles) used for analyzing TCL organics, TAL inorganics, and indicator parameters for the H.O.D Landfill Site will be prepared according to the procedures specified in U.S. EPA's Specifications and Guidance for Obtaining Contaminant-Free Sample Containers, April 1990. It will assure that the bottles used for the sampling activity do not contain contaminants exceeding the level specified in the above-mentioned document. Specifications for the bottles will be verified by checking the supplier's certified statement and analytical results for each bottle lot, and will be documented on a continuing basis. This data will be maintained in the project evidence file, and will be available, if requested, for EPA review.

In addition, the data for field blanks and trip blanks will be monitored for contamination, and corrective actions will be taken as soon as a problem is identified. This will be accomplished either by discontinuing the use of a specific bottle lot, contacting the bottle supplier(s) for retesting a representative bottle from a suspect lot, resampling the suspected samples, validating the data taking into account that the contaminants could be introduced by the laboratory (i.e., common lab solvents, sample handling artifacts, etc.) or could be a bottle QC problem, so as to make an educated determination of whether the bottles and hence the data are still usable, etc., whichever is appropriate.

SECTION 5

SAMPLE CUSTODY AND DOCUMENTATION

It is U.S. EPA policy to follow the U.S. EPA sample custody, or chain of custody protocols described in "NEIC Policies and Procedures", EPA-330/9-78-DDI-R, Revised June 1985. This custody is in three parts: sample collection, laboratory analysis, and final evidence files. Final evidence files, including all originals of laboratory reports and purge files, are maintained under document control in a secure area.

A sample or evidence file is under your custody if they:

- Are in your possession
- Are in your view, after being in your possession
- Are in your possession and you place them in a secured location
- Are in a designated secure area

5.1 Field Specific Custody Procedures

The sample packaging and shipment procedures summarized below will assure that the samples will arrive at the laboratory with the chain of custody intact. The protocol for sample designations are included in the SAP, Appendix A of this QAPjP.

5.1.1 Initiation of Chain of Custody Field Procedures

The field sampler is personally responsible for the care and custody of the samples until they are transferred or properly dispatched to the laboratory. As few people as possible should handle the samples. All bottles will be tagged with sample numbers and locations. Sample tags are to be completed for each sample using waterproof ink unless prohibited by weather conditions. For

example, a logbook notation would explain that a pencil was used to fill out the sample tag because the ballpoint pen would not function in freezing weather.

The RPM will review all field activities to determine whether proper custody procedures were followed during the field work and decide if additional samples are required.

5.1.2 Field Logbooks/Documentation

Field logbooks will provide the means of recording data collecting activities performed. As such, entries will be described in as much detail as possible so that persons going to the site could re-construct a particular situation without reliance on memory.

Field logbooks will be bound, field survey books or notebooks. Logbooks will be assigned to field personnel, but will be stored in the document control center when not in use. Each logbook will be identified by the project-specific document number.

The title page of each logbook will contain the following:

- Person to whom the logbook is assigned
- Logbook number
- Project name
- Project start date
- Project end date

Entries into the logbook will contain a variety of information. At the beginning of each entry, the date, start time, weather, names of all sampling team members present, level of personal protection being used, and the signature of the person making the entry will be entered. The names of visitors to the site, field sampling or investigation team personnel, and the purpose of their visit will also be recorded in the field logbook.

Measurements made and samples collected will be recorded. All entries will be made in ink, and no erasures will be made. If an incorrect entry is made, the information will be crossed out with a single strike mark, initialed, and dated by the person making the crossout. Whenever a sample is collected, or a measurement is made, a detailed description of the location of the station, which includes compass and distance measurements, shall be recorded. The number of the photographs taken of the station, if any, will also be noted. All equipment used to make measurements will be identified, along with the date of calibration.

Samples will be collected following the sampling procedures documented in the SAP, Appendix A of this QAPjP. The equipment used to collect samples will be noted, along with the time of sampling, sample description, depth at which the sample was collected, volume and number of containers. A sample identification number will be assigned prior to sample collection. Field duplicate samples, which will receive an entirely separate sample identification number, will be noted under sample description.

5.1.3 Transfer of Custody and Shipment Procedures

Samples are accompanied by a properly completed chain of custody form. The sample numbers and locations will be listed on the chain of custody form. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents transfer of custody of the samples from the sampler to another person to a mobile laboratory, to the permanent laboratory, or to/from a secure storage area.

Samples will be properly packaged for shipment and dispatched to the appropriate laboratory for analysis, with a separate signed custody record enclosed in each sample box or cooler. Shipping containers will be locked and secured with strapping tape and custody seals for shipment to the laboratory. The preferred procedure includes the use of a custody seal attached to the front right

and back left of the cooler. The custody seals are covered with clear plastic tape. The cooler is strapped shut with strapping tape in at least two locations.

Whenever samples are split with another source or government agency, a separate sample custody record is prepared for those samples, and marked to indicate with whom the samples are being split with. The person relinquishing the samples to the facility or agency should request the representatives signature acknowledging the sample receipt. If the representative is unavailable or refuses, the person relinquishing the samples should note this in the "received by" space of the custody form.

All shipments will be accompanied by the chain of custody record identifying the contents. The original record will accompany the shipment, and the pink and yellow copies will be retained by the sampler for returning to the sampling office.

If the samples are sent by common carrier, a bill of lading should be used. Receipts of bills of lading will be retained as part of the permanent documentation. If sent by mail, the package will be registered with return receipt requested. Commercial carriers are not required to sign off on the custody forms as long as the custody forms are sealed inside the sample cooler, and the custody seals remain intact. The person shipping the samples should note the carrier name and airbill number on the chain of custody record.

5.2 Laboratory Chain of Custody Procedures

Laboratory custody procedures for the sample receiving and log-in; sample storage; tracking during sample preparation and analysis; and storage of data are described in the individual laboratory custody SOPs provided in Appendix D.

5.3 Final Evidence File Custody Procedure

The final evidence file for the H.O.D. Landfill RI/FS will be located at and maintained by Warzyn. The content of the evidence file will include all relevant records, reports, correspondence, logs, field logbooks, laboratory sample preparation and analysis logbooks/documentation, analytical data packages, pictures, subcontractor reports, chain of custody records/forms, data review reports, etc. The evidence file will be under custody of the file custodian in a locked, secured area.

SECTION 6

CALIBRATION PROCEDURES AND FREQUENCY

This section describes procedures for maintaining the accuracy of all the instruments and measuring equipment which are used for conducting field tests and laboratory analyses. These instruments and equipment should be calibrated prior to each use or scheduled, periodic basis.

6.1 Field Instruments/Equipment

Instruments and equipment used to gather, generate, or measure environmental data will be calibrated with sufficient frequency and in such a manner that accuracy and reproducibility of results are consistent with the manufacturer's specifications.

Equipment to be used during the field sampling will be examined to certify that it is in operating condition. This includes checking the manufacturer's operating manual and the instruction and the instructions for each instrument to ensure that all maintenance requirements are being observed. Field notes from previous sampling trips will be reviewed so that the notation on any prior equipment problems are not overlooked, and all necessary repairs to equipment have been carried out.

Field instruments will be calibrated daily. Calibration procedures for field instruments are governed by the specific field SOPs provided in Appendix C. Field measurements include pH, conductivity, temperature, dissolved oxygen, redox potential, methane, oxygen, carbon dioxide, and Hnu screening of drill cuttings.

6.2 Laboratory Instruments

Procedures for the calibration of laboratory instruments must be established and maintained to ensure that equipment is functioning properly and that data collected are accurate and reliable. Requirements include step-by-step calibration procedures, frequency of re-calibration, equipment maintenance logs, instrument accuracy criteria, corrective action procedures and equipment limitations (e.g., working ranges), and are described, in detail, in the SOPs provided in Appendix B, and the SOWs for organics and inorganics.

SECTION 7

ANALYTICAL PROCEDURES

Groundwater, private/municipal well, surface water, soil/sediment, landfill gas, and leachate samples collected during field sampling activities for the H.O.D. Landfill Site RI will be analyzed by ETC, CompuChem, Enseco - Air Toxics Laboratory, Warzyn, and Core (see Table 1-1). Refer to Table 7-1 for a summary of analytical method references used for analysis.

7.1 Field Screening Analytical Protocols

The procedures for the field measurement of pH, conductivity, temperature, dissolved oxygen, redox potential, methane, oxygen and carbon dioxide are described in the SOPs provided in Appendix C.

7.2 Laboratory Analysis

Samples (groundwater, surface water, soil/sediment, and leachate samples) for CLP TCL organics and CLP TAL inorganics will be analyzed by ETC according to the analytical procedures set forth in the current CLP SOWs OLM01.8 for organics analysis, and ILM02.0 for inorganic analysis. Indicator parameters analyzed by Warzyn will follow the SOPs in Appendix B.

Low level TCL organic analysis of municipal/private wells by CompuChem will utilize the current low level CLP SOW OLC01.0. Low level TAL inorganic analysis for municipal/private wells analyzed by Warzyn will follow the SOPs set forth in Appendix B.

Landfill gas samples for volatiles will be analyzed by Enseco - Air Toxics Laboratory according to the SOP set forth in Appendix B.

Analysis of soil/sediments for physical characteristics will be performed by Warzyn (TOC for soil/sediment analyzed by ETC and clay mineralogy will be performed by Core Laboratories) using the methods provided in Appendix B.

SECTION 8

INTERNAL QUALITY CONTROL CHECK

8.1 Field Sample Collection

The assessment of field sampling precision and accuracy will be made through the collection of field duplicates and field blanks in accordance with the procedures described in the SAP (Appendix A of this QAPjP). Refer to Table 1-1 for a summary of sample numbers and required field QC samples.

8.2 Field Measurements

QC procedures for field measurements of pH, conductivity, temperature, dissolved oxygen, redox potential, methane, oxygen, and carbon dioxide are limited to checking the reproducibility of the measurements by obtaining multiple readings on a single sample or standard, and by calibrating the instruments. Refer to Table 3-7 for a summary of QC requirements.

8.3 Laboratory Analysis

The laboratories used for the analysis of samples for the H.O.D. Landfill Site (ETC, CompuChem, Enseco - Air Toxics Laboratory, Warzyn and Core Laboratories) have written QA/QC programs which provides rules and guidelines to ensure the reliability and validity of work conducted at the laboratory. Compliance with the QA/QC program is coordinated and monitored by the laboratory QAOs, which are independent of the operating departments. Laboratory procedures used are documented in writing and are provided or referenced in this QAPjP. Internal quality control checks are an integral part of the analytical methods, and are discussed in detail within the analytical procedures. The overall objectives of the internal quality control checks are to verify the established precision, accuracy and integrity of the methodology and to support the technical validity of the data. Where appropriate, internal quality control checks for analyses other than those following the CLP SOWs will include method blanks,

preparation/reagent blanks, calibration check samples, laboratory duplicates, matrix spikes and continuing calibration standards.

The required quality control frequency and performance criteria for TCL organics and TAL inorganics are summarized in the current CLP SOWs OLM01.8 and ILM02.0, respectively. The required QC frequency and performance criteria for low level organics are summarized in the current CLP SOW OLC01.0.

The required quality control frequency and performance criteria for the indicator parameters, landfill gas volatiles, physical characteristics, and low level TAL inorganics are summarized in Table 3-7.

The performing laboratories will document, in each data package provided, that both initial and ongoing instrument and analytical QC functions have been met. Any samples analyzed in non-conformance with the QC criteria set forth will be reanalyzed by the laboratory. It is expected that sufficient sample volume will be collected for re-analyses.

SECTION 9

DATA REDUCTION, VALIDATION AND REPORTING

9.1 Field Measurements and Sample Collection

Raw data from field measurements and sample collection activities will be appropriately recorded in the field logbook. Data will be reviewed to ensure procedures were followed and QC requirements were met, however, no formal data validation effort will be performed. If the data are to be used in the project reports, they will be reduced onto data summary tables.

9.2 Laboratory Services

9.2.1 Data Reduction

Each laboratory is responsible for identification, quantification, data reporting, and data deliverables for the analyses performed. Data reduction of TCL organic, low level TCL organic, and landfill gas volatile data will follow the requirements set forth in the CLP SOWs (OLM01.8 and OLC01.0). Data reduction of TAL inorganic, low level TAL inorganic, and indicators data will follow the requirements set forth in the CLP SOW ILM02.0. Deliverables will include raw data, summaries of calibration standards, duplicates, spikes, blanks, and performance evaluation samples.

9.2.2 Data Validation

Organic data (including low level TCL organics and landfill gas volatiles) generated under a DQO level of IV or V will be validated by Warzyn using Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, February 1988.

Inorganic data (including low level TAL inorganics) generated under a DQO level of IV will be validated by Warzyn using Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analyses, July 1988.

Indicator data generated under a DQO level of V will be validated by Warzyn using the Data Validation SOP provided in Appendix E.

Physical characteristic data (DQO level III) will be reviewed to ensure procedures were followed and QC requirements were met, however, no formal data validation effort will be performed.

Refer to Table 1-2 for a summary of data generating activities, intended data uses, and associated DQOs for the H.O.D. Landfill Site.

9.2.3 Data Reporting

Analytical data generated for the H.O.D. Landfill Site RI/FS will be computerized in a format organized to facilitate data review and evaluation. The computerized data set will include the data qualifiers provided by the performing laboratory in accordance with the CLP SOWs, as well as qualifiers added by the data reviewer in accordance with the data validation procedures noted in Section 9.2.2 of this QAPjP.

The laboratory-provided qualifiers will include such items as:

- Non-detects
- Concentration below required detection limit
- Estimated concentration due to poor QC data
- Concentration of chemical also found in the laboratory blank

The data review qualifiers will indicate whether the data are:

- Usable as a quantitative concentration
- Usable with caution as an estimated concentration
- Unusable due to out-of-control QC results

A summary of the validated data will be incorporated into the RI report.

SECTION 10

PERFORMANCE AND SYSTEM AUDITS

Performance and system audits of both field and laboratory activities will be conducted to verify that sampling and analysis are performed in accordance with the procedures established in the SAP and QAPjP. The audits of field and laboratory activities include two separate independent parts: internal and external audits.

10.1 Field Audits

10.1.1 Internal Audits

Internal audits of field activities (sampling and measurements) will be conducted by the Warzyn QAO and/or RI Leader. The purpose of the field audit will be to evaluate and document adherence to procedures described in the QAPjP and SAP. The audit will include review of field activities, sample documentation, chain of custody forms, field logbooks, and sampling and decontamination activities. Follow-up audits will be conducted to correct deficiencies, and to verify that QA procedures are maintained throughout the investigation.

10.1.2 External Audits

External audits conducted will be the responsibility of the U.S. EPA CRL and/or CDO.

10.2 Laboratory Audits

10.2.1 Internal Audits

The purpose of the internal laboratory audit is to evaluate and document adherence to analytical procedures described in this QAPjP. Internal audits of the participating laboratories are the responsibility of the individual laboratory QAO. System audits will include examination of laboratory documentation on sample receiving, sample log-in, sample storage, chain of custody procedure, sample preparation and analysis, instrument operating records, etc., and will be

performed annually. Performance audits consisting of blind QC samples prepared and submitted to the laboratory for analysis, will be performed quarterly. Results of these blind QC samples will be reviewed by the laboratory QAO.

10.2.2 External Audits

The U.S. EPA CRL will audit performing laboratories and provide recommendations for approval of the laboratory for the requested analyses to the U.S. EPA RPM. The audit may consist of a review of analytical and chain of custody procedures, evaluation of performance samples, and may also include an on-site audit of each participating laboratory.

SECTION 11
PREVENTATIVE MAINTENANCE

11.1 Field Instruments/Equipment

Field equipment used for this project include: thermometers, pH meter, conductivity meter, dissolved oxygen meter, redox meter, gas-tech meter, and sampling and filtering equipment. Specific preventative maintenance procedures to be followed for field equipment are those recommended by the manufacturer.

Field instruments will be checked and calibrated before they are transported to the field. These instruments will be checked and calibrated daily before use. Calibration checks will be performed as noted in Table 3-7 and will be recorded in the field logbook.

Critical spare parts such as electrodes, batteries, and pH probes will be kept on-site to minimize instrument down time. Backup instruments and equipment will be available within on-day shipment to avoid delays in the field schedule.

11.2 Laboratory Instruments

Preventative maintenance procedures for laboratory instrumentation and equipment for TCL organics (including low level TCL organics and landfill gas volatiles) are referenced in the current CLP SOWs OLM01.8 and OLC01.0. Preventative maintenance procedures for laboratory instrumentation and equipment for TAL inorganics (including low level TAL inorganics) are referenced in the current CLP SOW ILM02.0.

Preventative maintenance of laboratory instruments associated with the indicator parameters will be as directed with manufacturer's specifications, instrument operating procedures, and analytical methods. Maintenance is carried out on a regular, scheduled basis, and is documented in the instrument service logbook for each instrument. Emergency repair or scheduled manufacturer's maintenance is provided by an on-site technician or maintenance contract with the factory representatives.

SECTION 12

SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS

12.1 Field Measurements

Field data will be assessed by the Site QAO. The Site QAO will review the field results for compliance with the established QC criteria that are specified in the QAPjP and SAP. Accuracy of field measurements will be assessed using daily instrument calibration, calibration check, and blank data. Precision will be assessed on the basis of reproducibility by taking multiple readings of a single sample. Data completeness will be calculated as follows:

$$\text{Completeness} = \frac{\text{Valid Data Obtained}}{\text{Total Data Planned}} \times 100$$

12.2 Laboratory Data

12.2.1 Precision

Precision of laboratory analysis will be assessed by comparing the analytical results between MS/MSD for organic analysis, and laboratory duplicate analyses for inorganic and indicator analysis. The relative percent difference (RPD) will be calculated for each pair of duplicate analysis results as follows:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

where, S = first sample value (original or MS value)
D = Second sample value (duplicate or MSD value)

12.2.2 Accuracy

Accuracy of laboratory results will be assessed based on the established QC criteria that are described in Section 3 of this QAPjP, using the analytical results of method blanks, matrix spike samples, and field blanks. The percent recovery (%R) will be calculated as follows:

$$\%R = \frac{A - B}{C} \times 100$$

where, A = The analyte concentration determined experimentally from the spiked sample;
B = The background level determined by a separate analysis of the unspiked sample; and
C = The amount of the spike added.

12.2.3 Completeness

The data completeness of laboratory analysis results will be assessed for compliance with the amount of data required for decision making. Completeness is calculated by the following formula:

$$\text{Completeness} = \frac{\text{Valid Data Obtained}}{\text{Total Data Planned}} \times 100$$

12.2.4 Sensitivity

The achievement of method detection limits depend on instrument sensitivity and matrix effects. It is important to monitor the instrument sensitivity to ensure the data quality through constant instrument performance. The instrument sensitivity will be monitored through the analysis of method blanks, calibration check samples, and laboratory control samples.

SECTION 13
CORRECTIVE ACTION

Corrective actions may be required for two classes of problems: analytical and equipment problems, and noncompliance problems. Analytical and equipment problems may occur during sampling and sample handling, sample preparation, laboratory instrumental analysis, and data review.

For noncompliance problems, a formal corrective action program will be determined and implemented at the time the problem is identified. The person who identifies the problem is responsible for notifying the RPM. If the problem is analytical in nature, information on these problems will be promptly communicated to the U.S. EPA QAS. Implementation of corrective action will be confirmed in writing through the same channels.

Any nonconformance with the established quality control procedures in the QAPjP or SAP will be identified and corrected in accordance with the QAPjP. The U.S. EPA RPM, or his/her designee will issue a nonconformance report for each nonconformance condition.

Corrective actions will be implemented and documented in the field record book. No staff member will initiate corrective action without prior communication of findings through the proper channels. If corrective actions are insufficient, work may be stopped by stop-work order by the RPM.

13.1 Sample Collection/Field Measurements

Technical staff and project personnel will be responsible for reporting all suspected technical or QA nonconformances or suspected deficiencies of any activity or issued document by reporting the situation to the Warzyn RI Leader, or his/her designee. This manager will be responsible for

assessing the suspected problems in consultation with the Warzyn Project Manager on making a decision based on the potential for the situation to impact the quality of the data. If it is determined that the situation warrants a reportable nonconformance requiring corrective action, then a nonconformance report will be initiated by the manager.

The manager will be responsible for ensuring that corrective action for nonconformances are initiated by:

- Evaluating all reported nonconformances
- Controlling additional work on nonconforming items
- Determining disposition or action to be taken
- Maintaining a log of nonconformances
- Reviewing nonconformance reports and corrective actions taken
- Ensuring nonconformance reports are included in the final site documentation in the project files

If appropriate, the Warzyn Project Manager will ensure that no additional work that is dependent on the nonconforming activity is performed until the corrective actions are completed.

Corrective action for field measurements may include:

- Repeat the measurement to check the error
- Check for all proper adjustments for ambient conditions such as temperature
- Check the batteries
- Re-calibration
- Check the calibration
- Replace the instrument or measurement devices

- Stop work (if necessary)

The Warzyn RI Leader, or his/her designee, is responsible for all site activities. In this role, the Warzyn RI Leader, at times is required to adjust the site programs to accommodate the site-specific needs. When it becomes necessary to modify a program, the Warzyn RI Leader notifies the Warzyn Project Manager of the anticipated change and implements the necessary changes after obtaining the approval of the Project Manager. The change in the program will be documented and signed by the appropriate personnel.

The Warzyn RI Leader for the H.O.D. Landfill Site is responsible for the controlling, tracking, and implementation of the identified changes. Reports on all changes will be distributed to all affected parties, including the U.S. EPA RPM, the Warzyn Project Manager, and the WMII Project Manager.

13.2 Laboratory Analysis

Corrective actions are required whenever an out-of-control event or potential out-of-control event is noted. The investigative action taken is dependent on the analysis and the event. Laboratory personnel are alerted that corrective actions may be necessary if:

- QC data are outside the warning or acceptable windows for precision and accuracy
- Blanks contain target analytes above acceptable levels
- Undesirable trends are detected in spike recoveries or RPD between duplicates
- There are unusual changes in detection limits
- Deficiencies are detected by the QA Department during internal or external audits , or from the results of performance evaluation samples
- Inquiries concerning data quality are received

Corrective action procedures are often handled at the bench level, by the analyst who reviews the sample preparation procedure for possible errors and checks the instrument calibration, spike and calibration mixes, instrument sensitivity, etc. If the problem persists, or cannot be identified, the matter is referred to the laboratory supervisor, manager, or QAO for further investigation. Once resolved, full documentation of the corrective action procedure is filed with the QA Department.

SECTION 14

QUALITY ASSURANCE REPORTS TO MANAGEMENT

Reports will be submitted to the U.S. EPA and Illinois Environmental Protection Agency (IEPA) as described in Section 4.4.7, "Task 7: Reports" of the Work Plan. Reports will consist of monthly progress reports, technical memoranda, and the draft RI report.

Monthly progress reports submitted to the U.S. EPA and IEPA will include:

- A summary of the validated sampling and testing results
- A description of activities completed during the past month, as well as actions which are scheduled for the next month
- A summary of target and actual completion dates for each activity
- Changes in key personnel
- Problems encountered and how they were resolved
- Anticipated problems and recommended solutions

The results of specific RI activities such as the Risk Assessment, and Site Characterization will be submitted to the U.S. EPA and IEPA in the form of Draft Technical Memoranda. Technical Memoranda will include the following:

- Physical and Source Characterization Results
- Contaminant and Migration Pathways Characterization Results
- Baseline Risk Assessment

A draft RI Report summarizing the RI activities will be submitted to the U.S. EPA. The report will characterize the Site and summarize the data collected and conclusions. The RI report will not be considered final until Site characterization activities are complete for the supporting remedial alternatives screening activities and a letter of approval is issued by the U.S. EPA RPM.

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Table 1-1
Sample Type and Estimated Sample Numbers
H.O.D. Landfill RI/FS

Sample[1] Matrix	Lab[2]	No. of Samples	Field Duplicates	Field[3] Blanks	MS/MSD[4]	Total No. Samples	Test[5,6,7] Parameters	Field Parameters
PHYSICAL INVESTIGATION								
Soil borings	Warzyn Soils	16	2	-	-	18	Grain Size	
SOURCE CHARACTERIZATION								
Soils (clay cap)	Warzyn Soils	10	1	-	-	11	Grain Size, Atterberg Limits, Natural Moisture Content, and Density	
	Core	10	1	-	-	11	Clay Mineralogy	
Sediments/Surface Soils	ETC	5	1	-	1	6	TCL Organics	
	ETC	5	1	-	-	6	TAL Inorganics	
	ETC	5	1	-	-	6	TOC	
	Warzyn Soils	5	1	-	-	6	Grain Size, Natural Moisture Content, and Atterberg Limits	
Leachate	ETC	5	1	1	1	7	TCL Organics	pH, Conductivity,
	ETC	5	1	1	-	7	TAL Inorganics	Temperature, Redox,
	Warzyn Anayl	5	1	1	-	7	Indicators	and Dissolved Oxygen
Landfill Gas	Enseco - Air Toxics	5	1	1	-	7	VOCs	Methane, Oxygen, and Carbon Dioxide
Landfill Soil Borings	Warzyn Soils	10	1	-	-	11	Grain Size	
DEFINE NATURE AND EXTENT OF CONTAMINATION								
Groundwater - Upper	ETC	16	2	2	2	20	TCL Organics	pH, Conductivity,
and Lower Aquifers	ETC	16	2	2	-	20	TAL Inorganics	Temperature, Redox,
	Warzyn Anayl	16	2	2	-	20	Indicators	and Dissolved Oxygen
Municipal/Private Wells	CompuChem	8	1	1	1	10	LL TCL Organics	pH, Conductivity,
	Warzyn Analy	8	1	1	-	10	LL TAL Inorganics	Temperature
Surface Water	ETC	3	1	1	1	5	TCL Organics	pH, Conductivity,
	ETC	3	1	1	-	5	TAL Inorganics	Temperature, Redox, and Dissolved Oxygen

Table 1-1
(continued)

Notes:

1. Samples will be considered low concentration, and will be packaged and shipped accordingly.

2. ETC
284 Raritan Center Pkway
Edison, NJ 08818

Warzyn Soils Laboratory
505 Science Drive, Suite C
University Research Park
Madison, WI 53711

Core Laboratories
1875 Monetary Lane
Carrollton, TX 75006

Warzyn Analytical
One Science Court
Madison, WI 53711

CompuChem Laboratories
3808 Chapel Hill
Nelson Highway
Research Triangle
Park, NC 27709

Enseco - Air Toxics Laboratory
9537 Telstar Avenue
Suite 118
El Monte, CA 91731

3. A trip blank for VOC analysis will be included with each cooler shipped for aqueous (leachate, groundwater, surface water, municipal well, and private well) samples. Trip blanks are not included in the total number of samples. One trip blank (pre-cleaned SUMMA passivated canister) is required for the sampling of landfill gas vents for volatiles.

4. EXTRA VOLUME REQUIREMENT: Extra volume is required for the MS/MSD quality control requirement (triple volume for VOCs, double volume for SVOCs and Pest/PCBs) for aqueous samples. MS/MSDs are required for soil samples, however do not require that additional volume be collected in the field. Inorganics and general water quality indicator parameters require duplicate and spike analyses, however, do not require additional sample volume to meet the specified QC. MS/MSD samples are not included in the total number of samples.

5. Refer to Tables 3-1 and 3-2 for the TCL organic and TAL inorganic parameter lists and required detection limits. Indicator parameters consist of chloride, sulfate, alkalinity, hardness, nitrate-N, nitrite-N, ammonia-N, TOC, and TDS. See Table 3-5 landfill gas VOC list and detection limits and Table 3-6 for indicator, field measurement, and physical characteristic lists and associated detection limits.

6. Groundwater samples for metals analysis will be field filtered through a 0.45 micron filter within 15 minutes of sample collection, and prior to the addition of preservatives.

7. LL = Low level detection limits are required. Refer to Tables 3-3 and 3-4 for the low level TCL organic and TAL inorganic parameter lists and required detection limits. Municipal/Private Wells will be sampled by the Lake County Health Department.

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Table 1-2
Sample Quantities, Containers, Preservatives and Packaging Requirements
H.O.D. Landfill RI/FS

Analysis	Bottles and Jars	Preservation	Holding Time[1]	Volume of Samples	Shipping	Normal Packaging[2]
Low Concentration (Organics)						
Groundwater, Surface Water, and Municipal/Private Wells						
TCL Semi-volatiles	Two 1-Liter amber glass bottles	Iced to 4°C.	7 days to extraction, analysis within 40 days after extraction.	Fill bottle to neck	Shipped daily by overnight carrier	Vermiculite
TCL Pesticides/PCBs	Two 1-Liter amber glass bottles	Iced to 4°C.	7 days to extraction, analysis within 40 days after extraction.	Fill bottle to neck	Shipped daily by overnight carrier	Vermiculite
TCL Volatiles	Three 40-mL volatile organic analysis (VOA) vials (Four for municipal/private well samples).	1:1 HCL (2 drops/ vial), iced to 4°C.	14 days	Fill completely no headspace	Shipped daily by overnight carrier	Vermiculite
Leachate						
TCL Semi-volatiles	Two 1-Liter amber glass bottles	Iced to 4°C.	7 days to extraction, analysis within 40 days after extraction.	Fill bottle to neck	Shipped daily by overnight carrier	Vermiculite
TCL Pesticides/PCBs	Two 1-Liter amber glass bottles	Iced to 4°C.	7 days to extraction, analysis within 40 days after extraction.	Fill bottle to neck	Shipped daily by overnight carrier	Vermiculite
TCL Volatiles	Three 40-mL VOA vials	Iced to 4°C.	7 days	Fill completely no headspace	Shipped daily by overnight carrier	Vermiculite

Table 1-2
(continued)

Analysis	Bottles and Jars	Preservation	Holding Time[1]	Volume of Samples	Shipping	Normal Packaging[2]
Soil and Sediment						
TCL Semivolatiles	One 8-oz wide mouth glass jar	Iced to 4°C.	14 days to extraction, analysis within 40 days after extraction.	Fill 3/4 full	Shipped daily by overnight carrier	Vermiculite
TCL Pesticides/PCBs	One 8-oz wide mouth glass jar	Iced to 4°C.	14 days to extraction, analysis within 40 days after extraction.	Fill 3/4 full	Shipped daily by overnight carrier	Vermiculite
TCL Volatiles	Two 4-oz wide mouth glass jars	Iced to 4°C.	14 days	Fill completely no headspace	Shipped daily by overnight carrier	Vermiculite
Landfill Gas						
Volatiles	One 6-liter SUMMA passivated canister	Maintain <25°C	14 days	Fill as described in procedure	Shipped daily by overnight carrier	Vermiculite
Low Concentration (Inorganics)						
Groundwater						
Metals	One 1-liter high density polyethylene bottle	Field filter through 0.45 um filter. HNO_3 to pH<2. Iced to 4°C.	180 days (28 days for mercury)	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Cyanide	One 1-liter high density polyethylene bottle	Add NaOH to pH>12. Iced to 4°C.	14 days	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Private/Municipal Wells						
Metals	One 1-liter high density polyethylene bottle	HNO_3 to pH<2. Iced to 4°C.	180 days (28 days for mercury)	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Cyanide	One 1-liter high density polyethylene bottle	Add NaOH to pH>12. Iced to 4°C.	14 days	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite

Table 1-2
(continued)

Analysis	Bottles and Jars	Preservation	Holding Time[1]	Volume of Samples	Shipping	Normal Packaging[2]
Surface Water and Leachate						
Metals	One 1-liter high density polyethylene bottle	HNO_3 to pH<2. Iced to 4°C.	180 days (28 days for mercury)	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Cyanide	One 1-liter high density polyethylene bottle	Add NaOH to pH>12. Iced to 4°C.	14 days	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Soil and Sediment						
Metals and Cyanide	One 8-oz wide mouth glass jar	Iced to 4°C.	180 days (28 days for mercury, 14 days for cyanide)	Fill 3/4 full	Shipped daily by overnight carrier	Vermiculite (Med in cans/ vermiculite)
Water Quality Indicator Parameters						
Groundwater and Leachate						
Nitrate-N, Ammonia, and TOC	One 1-liter high density polyethylene bottle	H_2SO_4 to pH<2. Iced to 4°C.	28 days	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Hardness	One 500-ml high density polyethylene bottle	HNO_3 to pH<2. Iced to 4°C.	180 days	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
Alkalinity, Chloride, Sulfate, and Nitrite-N	One 1-liter high density polyethylene bottle	Iced to 4°C.	28 days (14 days alkalinity, 48 hours nitrite)	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite
TDS	One 500-mL polyethylene bottle	Field filter through 0.45 um filter. Iced to 4°C	7 days	Fill to shoulder of bottle	Shipped daily by overnight carrier	Vermiculite

Table 1-2
(continued)

Analysis	Bottles and Jars	Preservation	Holding Time[1]	Volume of Samples	Shipping	Normal Packaging[2]
Physical Characteristics						
Soil						
Grain size, moisture content, density, and atterberg limits	Four 8-oz wide mouth glass jars	NONE	Not established	Fill 3/4 full	Ship by carrier	Vermiculite
Clay Mineralogy	Two 8-oz wide mouth glass jars	NONE	Not established	Fill 3/4 full	Ship by carrier	Vermiculite
TOC	One 4-oz wide mouth glass jar	Iced to 4°C.	28 days	Fill 3/4 full	Ship by carrier	Vermiculite

Notes:
1. These are technical holding times, which are started from the day of sample collection.
2. The packing material should completely cushion the sample bottles - botttom, sides and top.

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Table 1-3
Summary of Data Generating Activities and Associated Quality Objectives
H.O.D. Landfill RI/FS

Activity	Description	Intended Data Usages	Parameters	Data Quality Objective	Anticipated No. of Investigative Samples
PHYSICAL INVESTIGATION					
Hydrogeologic Evaluation	Eight borings taken in areas specified in the Work Plan.	Confirm glacial stratigraphy.	Grain Size	Level III data	16
SOURCE CHARACTERIZATION					
Landfill Cap Evaluation	Collect samples of the clay cap.	Evaluate the effectiveness of the existing cap. Landfill cap evaluation will provide data used to perform percolation analysis.	Grain Size, Atterberg Limits, Natural Moisture Content, Density, and Clay Mineralogy	Level III data	10
On-site Surface Soil and Sediment Sampling	Collection of on-site surface soil/sediments in likely soil/sediment deposition areas.	Contaminant characterization.	TCL, TAL Grain Size, Atterberg Limits, TOC, and Natural Moisture Content	Level IV data Level III data	5
Leachate Sampling	Collection of leachate samples.	Chemically characterize the leachate composition.	TCL, TAL Indicators[1] pH, Conductivity, Temperature, Dissolved Oxygen, and Redox (field)	Level IV data Level V data Level II data	5 5 5
Landfill Gas Probe Installation	Installation of multi-stage landfill gas probes in the same borehole as each new leachate piezometer.	Assess methane gas production.	Methane, Oxygen, and Carbon Dioxide (field)	Level II data	up to 39 measurements per round
Landfill Gas Sampling	Collection of landfill gas from leachate piezometers and/or gas well flares.	Chemically characterize landfill gas, and assess the potential for contamination of air.	VOCs Methane, Oxygen, and Carbon Dioxide (field)	Level V data Level II data	5 5

Table 1-3
(continued)

Activity	Description	Intended Data Usages	Parameters	Data Quality Objective	Anticipated No. of Investigative Samples
Landfill Borings	Drill approximately five landfill borings along the southern perimeter of the "old" landfill.	Determine the subsurface conditions and evaluate the feasibility of constructing a barrier along the perimeter of the landfill to contain leachate.	Grain Size	Level III data	10
DEFINE NATURE AND EXTENT OF CONTAMINATION					
Monitoring Well Installation	Hnu screening of drill cuttings	Determine cuttings to be drummed	Total VOCs >10 ppm	Level I data	0
Groundwater Monitoring	Obtain water level measurements. Conduct in-situ hydraulic conductivity tests. Install new wells, and sample and analyze the existing and new monitoring wells.	Evaluate potential groundwater flow paths, confirm hydraulic conductivity results with previous data, assess groundwater contamination migration pathway, and characterize groundwater quality.	TCL, TAL Indicators' pH, Conductivity, Temperature, Dissolved Oxygen, and Redox (field)	Level IV data Level V data Level II data	16 16 16
Municipal/Private Well Monitoring	Sampling private and municipal wells in the vicinity of the Site. Sampling to be performed by Lake County Health Department.	Characterize the water quality.	Low level TCL and TAL pH, Conductivity, and Temperature	Level IV data Level II data	8 8
Hydrologic Evaluation/Surface Water Sampling	Measure the surface water levels, flow, and inspect the Sequoit Creek banks.	Evaluate the potential for surface water contamination and characterize the surface water quality.	TCL, TAL pH, Conductivity, Temperature, Dissolved Oxygen, and Redox (field)	Level IV data Level II data	3 3

Notes:
1. Indicator parameters consist of: chloride, sulfate, alkalinity, hardness, nitrate-N, nitrite-N, ammonia, TOC, and TDS.
2. Grain Size = Sieve plus Hydrometer Analyses

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[mad-406-77b]
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Table 3-1
Target Compound List
and Contract Required Quantitation Limits - Organics

	Compound	Quantitation Limits[1] Water (ug/l)	Low Soil (ug/kg)	Medium Soil (ug/kg)
	Volatiles			
1.	Chloromethane	10	10	1200
2.	Bromomethane	10	10	1200
3.	Vinyl chloride	10	10	1200
4.	Chloroethane	10	10	1200
5.	Methylene chloride	10	10	1200
6.	Acetone	10	10	1200
7.	Carbon disulfide	10	10	1200
8.	1,1-Dichloroethene	10	10	1200
9.	1,1-Dichloroethane	10	10	1200
10.	1,2-Dichloroethene (total)	10	10	1200
11.	Chloroform	10	10	1200
12.	1,2-Dichloroethane	10	10	1200
13.	2-Butanone	10	10	1200
14.	1,1,1-Trichloroethane	10	10	1200
15.	Carbon tetrachloride	10	10	1200
16.	Bromodichloromethane	10	10	1200
17.	1,2-Dichloropropane	10	10	1200
18.	cis-1,3-Dichloropropene	10	10	1200
19.	Trichloroethene	10	10	1200
20.	Dibromochloromethane	10	10	1200
21.	1,1,2-Trichloroethane	10	10	1200
22.	Benzene	10	10	1200
23.	trans-1,3-Dichloropropene	10	10	1200
24.	Bromoform	10	10	1200
25.	4-Methyl-2-pentanone	10	10	1200
26.	2-Hexanone	10	10	1200
27.	Tetrachloroethene	10	10	1200
28.	Toluene	10	10	1200
29.	1,1,2,2-Tetrachloroethane	10	10	1200
30.	Chlorobenzene	10	10	1200
31.	Ethylbenzene	10	10	1200
32.	Styrene	10	10	1200
33.	Xylenes (total)	10	10	1200

Table 3-1
(continued)

	Compound	Quantitation Limits[1] Water (ug/l)	Low Soil (ug/kg)	Medium Soil (ug/kg)
	Semi-volatiles			
34.	Phenol	10	330	10000
35.	bis(2-Chloroethyl) ether	10	330	10000
36.	2-Chlorophenol	10	330	10000
37.	1,3-Dichlorobenzene	10	330	10000
38.	1,4-Dichlorobenzene	10	330	10000
39.	1,2-Dichlorobeznene	10	330	10000
40.	2-Methylphenol	10	330	10000
41.	2,2'-oxybis-(1-Chloropropane)	10	330	10000
42.	4-Methylphenol	10	330	10000
43.	n-Nitroso-di-n-dipropylamine	10	330	10000
44.	Hexachloroethane	10	330	10000
45.	Nitrobenzene	10	330	10000
46.	Isophorone	10	330	10000
47.	2-Nitrophenol	10	330	10000
48.	2,4-Dimethylphenol	10	330	10000
49.	bis(2-Chloroethoxy) methane	10	330	10000
50.	2,4-Dichlorophenol	10	330	10000
51.	1,2,4-Trichlorobenzene	10	330	10000
52.	Naphthalene	10	330	10000
53.	4-Chloroaniline	10	330	10000
54.	Hexachlorobutadiene	10	330	10000
55.	4-Chloro-3-methylphenol	10	330	10000
56.	2-Methylnaphthalene	10	330	10000
57.	Hexachlorocyclopentadiene	10	330	10000
58.	2,4,6-Trichlorophenol	10	330	10000
59.	2,4,5-Trichlorophenol	25	800	25000
60.	2-Chloronaphthalene	10	330	10000
61.	2-Nitroaniline	25	800	25000
62.	Dimethylphthalate	10	330	10000
63.	Acenaphthylene	10	330	10000
64.	2,6-Dinitrotoluene	10	330	10000
65.	3-Nitroaniline	25	800	25000
66.	Acenaphthene	10	330	10000
67.	2,4-Dinitrophenol	25	800	25000
68.	4-Nitrophenol	25	800	25000

Table 3-1
(continued)

	Compound	Quantitation Limits[1] Water (ug/l)	Low Soil (ug/kg)	Medium Soil (ug/kg)
69.	Dibenzofuran	10	330	10000
70.	2,4-Dinitrotoluene	10	330	10000
71.	Diethylphthalate	10	330	10000
72.	4-Chlorophenyl-phenyl ether	10	330	10000
73.	Fluorene	10	330	10000
74.	4-Nitroaniline	25	800	25000
75.	4,6-Dinitro-2-methylphenol	25	800	25000
76.	n-Nitrosodiphenylamine	10	330	10000
77.	4-Bromophenyl-phenyl ether	10	330	10000
78.	Hexachlorobenzene	10	330	10000
79.	Pentachlorophenol	25	800	25000
80.	Phenanthrene	10	330	10000
81.	Anthracene	10	330	10000
82.	Carbazole	10	330	10000
83.	Di-n-butylphthalate	10	330	10000
84.	Fluoranthene	10	330	10000
85.	Pyrene	10	330	10000
86.	Butylbenzylphthalate	10	330	10000
87.	3,3'-Dichlorobenzidine	10	330	10000
88.	Benzo(a)anthracene	10	330	10000
89.	Chrysene	10	330	10000
90.	bis(2-Ethylhexyl)phthalate	10	330	10000
91.	Di-n-ocylphthalate	10	330	10000
92.	Benzo(b)fluoranthene	10	330	10000
93.	Benzo(k)fluoranthene	10	330	10000
94.	Benzo(a)pyrene	10	330	10000
95.	Indeno(1,2,3-cd)pyrene	10	330	10000
96.	Dibenzo(a,h)anthracene	10	330	10000
97.	Benzo(g,h,i)perylene	10	330	10000

Table 3-1
(continued)

	Compound	Quantitation Limits[1] Water (ug/l)	Low Soil (ug/kg)	Medium Soil (ug/kg)
	Pesticides/PCBs			
98.	alpha-BHC	0.05	1.7	1.7
99.	beta-BHC	0.05	1.7	1.7
100.	delta-BHC	0.05	1.7	1.7
101.	gamma-BHC (Lindane)	0.05	1.7	1.7
102.	Heptachlor	0.05	1.7	1.7
103.	Aldrin	0.05	1.7	1.7
104.	Heptachlor epoxide	0.05	1.7	1.7
105.	Endosulfan I	0.05	1.7	1.7
106.	Dieldrin	0.10	3.3	3.3
107.	4,4'-DDE	0.10	3.3	3.3
108.	Endrin	0.10	3.3	3.3
109.	Endosulfan II	0.10	3.3	3.3
110.	4,4'-DDD	0.10	3.3	3.3
111.	Endosulfan sulfate	0.10	3.3	3.3
112.	4,4'-DDT	0.10	3.3	3.3
113.	Methoxychlor	0.50	17	17
114.	Endrin ketone	0.10	3.3	3.3
115.	Endrin aldehyde	0.10	3.3	3.3
116.	alpha-Chlordane	0.05	1.7	1.7
117.	gamma-Chlordane	0.05	1.7	1.7
118.	Toxaphene	5.0	170	170
119.	Aroclor-1016	1.0	33	33
120.	Aroclor-1221	2.0	67	67
121.	Aroclor-1232	1.0	33	33
122.	Aroclor-1242	1.0	33	33
123.	Aroclor-1248	1.0	33	33
124.	Aroclor-1254	1.0	33	33
125.	Aroclor-1260	1.0	33	33

Notes:

1. Quantitation limits listed for soil/sediment are based on wet weight. The quantitation limits calculated by the laboratory for soil/sediment, calculated on a dry weight basis as required by the method, will be higher.

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Table 3-2
Target Analyte List and
Contract Required Detection Limits - Inorganics

	Analyte	Contract Required [1,2,3] Detection Limit (ug/L)
1.	Aluminum	200
2.	Antimony	60
3.	Arsenic	10
4.	Barium	200
5.	Beryllium	5
6.	Cadmium	5
7.	Calcium	5000
8.	Chromium	10
9.	Cobalt	50
10.	Copper	25
11.	Iron	100
12.	Lead	3
13.	Magnesium	5000
14.	Manganese	15
15.	Mercury	0.2
16.	Nickel	40
17.	Potassium	5000
18.	Selenium	5
19.	Silver	10
20.	Sodium	5000
21.	Thallium	10
22.	Vanadium	50
23.	Zinc	20
24.	Cyanide	10

Notes:

1. Subject to the restrictions specified in the first page of Part G, Section IV of Exhibit D (Alternate Methods - Catastrophic Failure) any analytical method specified in SOW ILM02.0, Exhibit D, may be utilized as long as the documented instrument or method detection limits meet the Contract Required Detection Limit (CRDL) requirements. Higher detection limits may only be used in the following circumstance:

   If the sample concentration exceeds five times the detection limit of the instrument or method in use, the values

Table 3-2
(continued)

may be reported even though the instrument or method detection limit may not equal the CRDL. This is illustrated in the example below:

For lead:
Method in use = ICP
Instrument Detection Limit (IDL) = 40
Sample concentration = 200
CRDL = 3

The value of 200 may be reported even though the instrument detection limit is greater than the CRDL. The instrument or method detection limit must be documented as described in SOW ILM02.0, Exhibit E.

2. The CRDL are the instrument detection limits obtained in pure water that must be met using the procedure in Exhibit E. The detection limits for samples may be considerably higher depending on the sample matrix. Soil/sediment detection limits are approximately 200 times the CRDLs noted for water, and may vary as the soil/sediment results are reported on a dry weight basis. Soil/sediment results are reported in mg/kg.

3. This table is extracted from the Inorganic SOW ILM02.0 (Exhibit C).

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Table 3-3
Target Compound List
and Contract Required Quantitation Limits
Low Concentration Water Organics

	Compound	Quantitation Limits[1] Water (ug/L)
	Volatiles	
1.	Chloromethane	1
2.	Bromomethane	1
3.	Vinyl chloride	1
4.	Chloroethane	1
5.	Methylene chloride	2
6.	Acetone	5
7.	Carbon disulfide	1
8.	1,1-Dichloroethene	1
9.	1,1-Dichloroethane	1
10.	cis-1,2-Dichloroethene	1
11.	trans-1,2-Dichloroethene	1
12.	Chloroform	1
13.	1,2-Dichloroethane	1
14.	2-Butanone	5
15.	Bromochloromethane	1
16.	1,1,1-Trichloroethane	1
17.	Carbon tetrachloride	1
18.	Bromodichloromethane	1
19.	1,2-Dichloropropane	1
20.	cis-1,3-Dichloropropene	1
21.	Trichloroethene	1
22.	Dibromochloromethane	1
23.	1,1,2-Trichloroethane	1
24.	Benzene	1
25.	trans-1,3-Dichloropropene	1
26.	Bromoform	1
27.	4-Methyl-2-pentanone	5
28.	2-Hexanone	5
29.	Tetrachloroethene	1
30.	1,1,2,2-Tetrachloroethane	1
31.	1,2-Dibromomethane	1
32.	Toluene	1
33.	Chlorobenzene	1
34.	Ethylbenzene	1
35.	Styrene	1

Table 3-3
(continued)

	Compound	Quantitation Limits' Water (ug/L)
36.	Xylenes (total)	1
37.	1,3-Dichlorobenzene	1
38.	1,4-Dichlorobenzene	1
39.	1,2-Dichlorobenzene	1
40.	1,2-Dibromo-3-chloropropane	1
	Semi-volatiles	
41.	Phenol	5
42.	bis(2-Chloroethyl) ether	5
43.	2-Chlorophenol	5
44.	2-Methylphenol	5
45.	2,2'-oxybis-(1-Chloropropane)	5
46.	4-Methylphenol	5
47.	n-Nitroso-di-n-dipropylamine	5
48.	Hexachloroethane	5
49.	Nitrobenzene	5
50.	Isophorone	5
51.	2-Nitrophenol	5
52.	2,4-Dimethylphenol	5
53.	bis(2-Chloroethoxy) methane	5
54.	2,4-Dichlorophenol	5
55.	1,2,4-Trichlorobenzene	5
56.	Naphthalene	5
57.	4-Chloroaniline	5
58.	Hexachlorobutadiene	5
59.	4-Chloro-3-methylphenol	5
60.	2-Methylnaphthalene	5
61.	Hexachlorocyclopentadiene	5
62.	2,4,6-Trichlorophenol	5
63.	2,4,5-Trichlorophenol	20
64.	2-Chloronaphthalene	5
65.	2-Nitroaniline	20
66.	Dimethylphthalate	5
67.	Acenaphthylene	5
68.	2,6-Dinitrotoluene	5
69.	3-Nitroaniline	20
70.	Acenaphthene	5

Table 3-3
(continued)

	Compound	Quantitation Limits[1] Water (ug/L)
71.	2,4-Dinitrophenol	20
72.	4-Nitrophenol	20
73.	Dibenzofuran	5
74.	2,4-Dinitrotoluene	5
75.	Diethylphthalate	5
76.	4-Chlorophenyl-phenyl ether	5
77.	Fluorene	5
78.	4-Nitroaniline	20
79.	4,6-Dinitro-2-methylphenol	20
80.	n-Nitrosodiphenylamine	5
81.	4-Bromophenyl-phenyl ether	5
82.	Hexachlorobenzene	5
83.	Pentachlorophenol	20
84.	Phenanthrene	5
85.	Anthracene	5
86.	Di-n-butylphthalate	5
87.	Fluoranthene	5
88.	Pyrene	5
89.	Butylbenzylphthalate	5
90.	3,3'-Dichlorobenzidine	5
91.	Benzo(a)anthracene	5
92.	Chrysene	5
93.	bis(2-Ethylhexyl)phthalate	5
94.	Di-n-ocylphthalate	5
95.	Benzo(b)fluoranthene	5
96.	Benzo(k)fluoranthene	5
97.	Benzo(a)pyrene	5
98.	Indeno(1,2,3-cd)pyrene	5
99.	Dibenzo(a,h)anthracene	5
100.	Benzo(g,h,i)perylene	5
	Pesticides/PCBs	
101.	alpha-BHC	0.01
102.	beta-BHC	0.01
103.	delta-BHC	0.01
104.	gamma-BHC (Lindane)	0.01
105.	Heptachlor	0.01

Table 3-3
(continued)

	Compound	Quantitation Limits[1] Water (ug/L)
106.	Aldrin	0.01
107.	Heptachlor epoxide	0.01
108.	Endosulfan I	0.01
109.	Dieldrin	0.02
110.	4,4'-DDE	0.02
111.	Endrin	0.02
112.	Endosulfan II	0.02
113.	4,4'-DDD	0.02
114.	Endosulfan sulfate	0.02
115.	4,4'-DDT	0.02
116.	Methoxychlor	0.10
117.	Endrin ketone	0.02
118.	Endrin aldehyde	0.02
119.	alpha-Chlordane	0.01
120.	gamma-Chlordane	0.01
121.	Toxaphene	1.0
122.	Aroclor-1016	0.20
123.	Aroclor-1221	0.20
124.	Aroclor-1232	0.40
125.	Aroclor-1242	0.20
126.	Aroclor-1248	0.20
127.	Aroclor-1254	0.20
128.	Aroclor-1260	0.20

Notes:
1. This table was extracted from the low level detection SOW OLC01.0.

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TABLE 3-4

Target Analyte List and Required Detection Limits Low Concentration Water Inorganics

	Analyte	Required Detection Limit (ug/L)
1.	Aluminum	50
2.	Antimony	5
3.	Arsenic	2
4.	Barium	10
5.	Beryllium	5
6.	Cadmium	0.2
7.	Calcium	1000
8.	Chromium	0.2
9.	Cobalt	10
10.	Copper	10
11.	Iron	20
12.	Lead	3
13.	Magnesium	1000
14.	Manganese	10
15.	Mercury	0.2
16.	Nickel	20
17.	Potassium	100
18.	Selenium	2
19.	Silver	0.5
20.	Sodium	1000
21.	Thallium	3
22.	Vanadium	2
23.	Zinc	10
24.	Cyanide	10

NOTES: Refer to Appendix B-9 for method references.

TABLE 3-5

Landfill Gas Volatile Organic List and Required Detection Limits

Volatile Compound	Required Detection ppb (vol/vol)
Dichlorodifluoromethane	2
Chloromethane	2.5
1,2-Dichloro-1,1,2,2-Tetrafluoroethane	2
Vinyl Chloride	2.5
Bromomethane	3
Chloroethane	5
Trichlorofluoromethane	1
cis-1,2-Dichloroethene	2
Carbon Disulfide	10
1,1,2-Trichloro-1,2,2-Trifluoroethane	2
Acetone	10
Methylene Chloride	4
trans-1,2-Dichloroethene	4
Hexane	8
1,1-Dichloroethane	2.5
Vinyl Acetate	2.5
1,1-Dichloroethene	2
2-Butanone	3
Chloroform	2
1,1,1-Trichloroethane	2
Carbon Tetrachloride	2
Benzene	3
1,2-Dichloroethane	2
Trichloroethene	2.5
1,2-Dichloropropane	8
1,4-Dioxane	7
Bromodichloromethane	2
cis-1,3-Dichloropropene	3
4-Methyl-2-Pentanone	3
Toluene	3

TABLE 3-5
(continued)

Volatile Compound	Required Detection ppb (vol/vol)
trans-1,3-Dichloropropene	3
1,1,2-Trichloroethane	3
Tetrachloroethene	3
2-Hexanone	5
Dibromochloromethane	3
1,2-Dibromomethane	2
Chlorobenzene	2.5
Ethylbenzene	2.5
Total Xylenes	5
Styrene	7
Bromoform	2
1,1,2,2-Tetrachloroethane	4
Benzyl Chloride	2
4-Ethyl Toluene	4
1,3,5-Trimethylbenzene	2.5
1,2,4-Trimethylbenzene	3
1,3-Dichlorobenzene	3
1,4-Dichlorobenzene	4
1,2-Dichlorobenzene	5
1,2,4-Trichlorobenzene	7
Hexachlorobutadiene	5

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TABLE 3-6

Indicators, Field Measurements, and Physical Characteristics Parameter Lists and Required Detection Limits

Indicator Parameter	Required Detection Limit (mg/L)
Alkalinity	10
Chloride	2
Hardness	10
Sulfate	10
Total Organic Carbon	1.0
Total Dissolved Solids	10
Nitrate Nitrogen	0.02
Nitrite Nitrogen	0.02
Ammonia Nitrogen	0.10

Field Measurement Parameter	Required Detection Limit
pH (s.u.)	to nearest 0.05 pH unit
Conductivity @25 Deg. C (umhos/cm)	10
Temperature (Deg. C)	to nearest 0.5 degree
Redox Potential (mV)	to nearest 1 mV
Dissolved Oxygen (mg/L)	1
Oxygen (%)	1
Methane (%)	1
Carbon Dioxide (%)	1
Total VOCs (Hnu screening PPM)	1

Physical Characteristic Parameter	Required Detection Limit
Grain Size	-
Atterberg Limits	-
Natural Moisture Content (%)	0.1
Density	-
Total Organic Carbon (mg/kg)	100
Clay Mineralogy by X-ray Diffraction (weight percent of fraction analyzed)	1

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[CHI-402-77h]
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TABLE 3-7

Summary of Quality Control Requirements
H.O.D. Landfill Site RI/FS

Parameter	Audit[1]	Frequency[2]	Quality Control[3] Criteria
TCL Organics	Requirements per OLM01.8 (or most current)		
TAL Inorganics	Requirements per ILM02.0 (or most current)		
Low Level TCL Organics	Requirements per OLC01.0 (or most current)		
Low Level TAL Inorganics	Requirements per ILM02.0 (or most current)		
Landfill Gas Volatiles	GC-MS Tune	1 per day	Per Section 8.2 of SOP (Appendix B-11 of QAPP)
	Check Standard	1 per day	±30% of initial calibration
	LCS	1 per day	80 - 115%
	DCS	1 per day	80 - 115%
	Methanol Blank	1 per day	<DL
Alkalinity, Hardness, Nitrite, Nitrate, Chloride, and Sulfate	Lab Blank (ICB, CCB)	1 per 10 samples and at end of run	< Detection Limit (DL)
	Check Standard (ICV, CCV)	1 per 10 samples and end of run	90-110% Recovery
	EPA QC Reference Standard	1 per set	80-120% Recovery
	Lab Duplicate	1 per 10 samples	10 RPD (±2xDL if sample concentration is <5xDL)
	Matrix Spike	1 per 10 samples	85-115% Recovery
TOC (water)	Lab Blank (ICB, CCB)	1 per 10 samples and at and of run	<DL
	EPA QL References Standard	1 per set	80-120%. Recovery.
	Check Standard (ICV, CCV)	1 per 10 samples and end of run	90-110% Recovery
	Lab Duplicate	1 per 10 samples	10 RPD (±2xDL if sample concentration is <5xDL)
	Matrix Spike	1 per 10 samples	80-120% Recovery

TABLE 3-7
(continued)

Parameter	Audit[1]	Frequency[2]	Quality Control[3] Criteria
TOC (soil)	Lab Blank	1 per run	<DL
	Calibration Check Standards	4 per run	10% of initial calibration
	EPA QC Reference	1 per run	EPA criteria
Total Dissolved Solids	Lab Blank	1 per set	<DL
	EPA QC Reference Standard	1 per set	80-120% Recovery,
	Lab Duplicate	1 per 10 samples	10% RPD (± 2xDL if sample concentration is <5 x DL)
Ammonia Nitrogen	Lab Blank (ICB, CCB)	1 per 10 samples and at end of run	<DL
	Check Standard (ICV, CCV)	1 per 10 samples and at end of run	90-110% Recovery
	EPA QC Reference Standard	1 per set	80-120% Recovery
	Preparation Blank	1 per set	<DL
	Lab Duplicate	1 per 10 samples	10% RPD (± 2xDL if sample concentration is <5 x DL)
	Matrix Spike	1 per 10 samples	80 - 120% Recovery
Grain Size, Natural Moisture Content, Atterberg Limits, and Density	Lab Duplicate	1 per 10 samples	40% RPD or <2% by weight
pH (Field)	Check Standard	1 per 10 samples	± 0.05 pH unit of buffer selection
	Duplicate	1 per 10 samples	± 0.2 pH unit

TABLE 3-7
(continued)

Parameter	Audit[1]	Frequency[2]	Quality Control[3] Criteria
Specific Conductance (Field)	Check Standard	1 per 10 samples	± 10% of standard
	Duplicate	1 per 10 samples	15% RPD (± 2xDL if sample concentration is <5 x DL)
Temperature (Field)	Duplicate	1 per 10 samples	20% RPD
Dissolved Oxygen (Field)	Duplicate	1 per 10 samples	20% RPD
Redox Potential (Field)	Check Standard	1 per 5 samples	± 10 MV of true value
	Duplicate	1 per 10 samples	20% RPD
Methane, Oxygen and Carbon Dioxide (Field)	Duplicate	1 per 10 samples	20% RPD
Total VOCs (HNU Field)	Duplicate	1 per 10 samples	20% RPD

Notes:
1. LCS = Laboratory control spike
   DCS = Duplicate control spike(s)
   CCV = Continuing Calibration Check Standard
   ICV = Initial Calibration Check Standard
   CCB = Continuing Calibration Blank
   ICB = Initial Calibration Blank
2. Frequencies apply to each individual matrix.
3. DL = Detection Limit and RPD = Relative Percent Difference. Refer to Tables 3-1, 3-2, 3-3, 3-4, 3-5, and 3-6 for required detection limits for each analyte.

CAW/ndj/JAH
[CHI-402-77i]
6095300/154

Table 7-1
Summary of Analytical Methods
H.O.D. Landfill RI/FS

Parameter	SOP[1]	Method[2]
TCL Volatiles	SOW OLM01.8	EPA 624
TCL Semi-volatiles	SOW OLM01.8	EPA 625
TCL Pesticides/PCBs	SOW OLM01.8	EPA 608
TCL Volatiles (Low level detection)	SOW OLC01.0	EPA 524.2
TCL Semi-volatiles (Low level detection)	SOW 0LC01.0	EPA 625
TCL Pesticides/PCBs (Low level detection)	SOW 0LC01.0	EPA 608
Landfill Gas Volatiles	CRL-LM-7001	EPA Compendium Method TO-14
TAL Inorganics	SOW ILM02.0	EPA 200.7 (ICP) EPA 200 (AA) EPA 245 (Mercury) EPA 335 (Cyanide)
TAL Inorganics (Low level detection)	SOW ILM02.0 plus SOPs in Appendix B	EPA 200.7 (ICP) EPA 200 (AA) EPA 245 (Mercury) EPA 335 (Cyanide)
Alkalinity	LAAC,ALKAAC3	EPA 310.2
Hardness	LAAC, HARDAAC2	EPA 130.1
Ammonia Nitrogen	NH3DTC	EPA 350.2
Total Dissolved Solids	TDSC3	EPA 160.1
Chloride	LAAC, CLAAC2	EPA 325.2
Sulfate	LAAC, S04AAC3	EPA 375.2
Nitrate Nitrogen	LAAC, NO2+NO3AAC2	EPA 353.2
Nitrite Nitrogen	LAAC,NO2AAC2	EPA 354.1
Total Organic Carbon (water)	TOCIOPC, TOC3C	EPA 415.1
Total Organic Carbon (soil)	ED522902	EPA 415.1 and SW846 9060

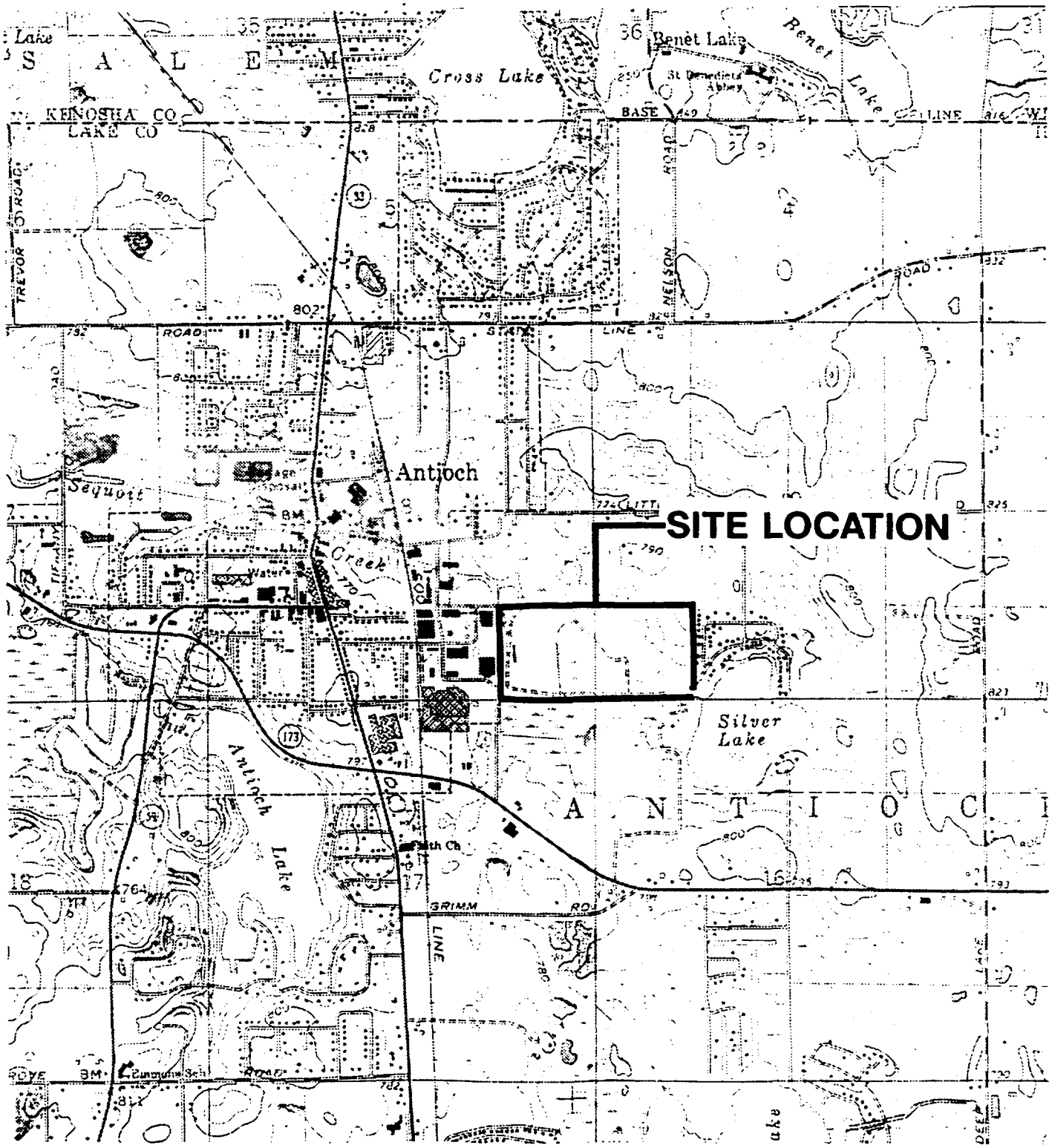
Table 7-1
(continued)

Field Measurements		
pH	pH	EPA 150.1
Specific conductance	CONDYSI	EPA 120.1
Temperature	TEMPFC	EPA 170.1
Redox potential	REDOX	Bechman pH Meter Instruction Manual
Dissolved Oxygen	YSIDO	YSI Meter Instruction Manual
Methane and Oxygen	GASTECHTOR	Gastech Model 1939 Instruction Manual
Carbon Dioxide	-	Sensidyne Instruction Manual
Physical Characteristics		
Grain Size Analysis	-	ASTM D422, D1140
Atterberg Limits	-	ASTM D4318, D427
Natural Moisture Content	-	ASTM D2216
Density	-	ASTM D854
Clay Mineralogy	-	Refer to SOP in Appendix B

Footnotes:

(1) SOP - Standard Operating Procedures refers to either the EPA Statement of Work (SOW) or the appropriate laboratory document number.

(2) Method refers to the published analytical reference.



north

0 2000 4000

SCALE IN FEET

NOTES

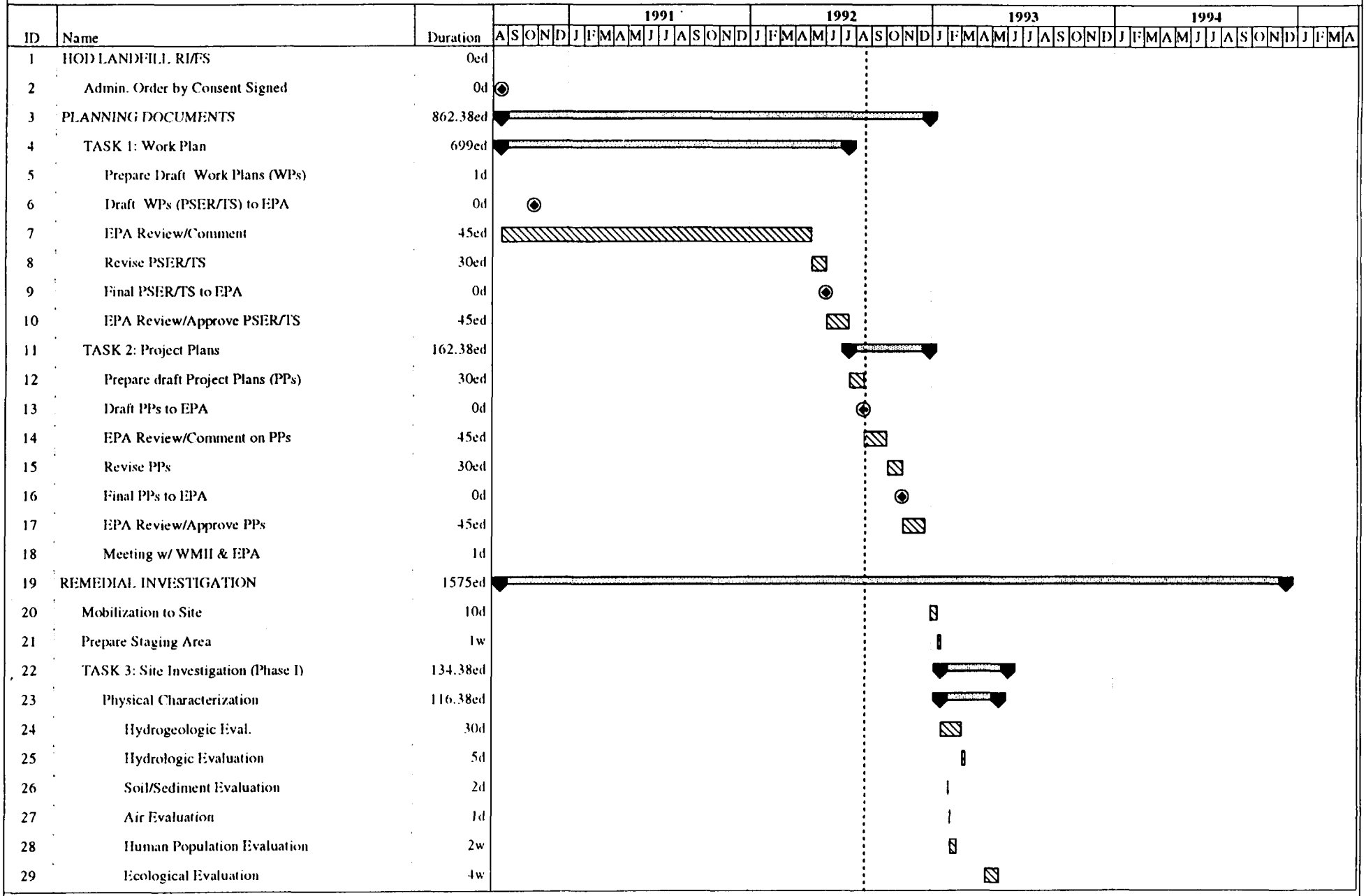
1. SITE LOCATION MAP DEVELOPED FROM THE ANTIOCH, ILLINOIS 7 1/2 MINUTE U.S.G.S. TOPOGRAPHIC QUADRANGLE MAP, DATED 1960, PHOTOREVISED 1972.

FIGURE 1-1

WARZYN	SITE LOCATION MAP	Drawn HLH	Checked RJM	App'd. AJS
	PRELIMINARY SITE EVALUATION REPORT H.O.D. LANDFILL, RI/FS ANTIOCH, ILLINOIS	Revisions		Date 10/24/90 60953 A1

Drafting Standards DLF 10-22-90 PM Division GWH
Lead Professional AJS Other
Section RM

FIGURE 1-2
H.O.D. LANDFILL RI/FS
ANTIOCH, ILLINOIS



ID	Name	Duration
1	HOD LANDFILL RI/FS	0ed
2	Admin. Order by Consent Signed	0d
3	PLANNING DOCUMENTS	862.38ed
4	TASK 1: Work Plan	699ed
5	Prepare Draft Work Plans (WPs)	1d
6	Draft WPs (PSER/TS) to EPA	0d
7	EPA Review/Comment	45ed
8	Revise PSER/TS	30ed
9	Final PSER/TS to EPA	0d
10	EPA Review/Approve PSER/TS	45ed
11	TASK 2: Project Plans	162.38ed
12	Prepare draft Project Plans (PPs)	30ed
13	Draft PPs to EPA	0d
14	EPA Review/Comment on PPs	45ed
15	Revise PPs	30ed
16	Final PPs to EPA	0d
17	EPA Review/Approve PPs	45ed
18	Meeting w/ WMII & EPA	1d
19	REMEDIAL INVESTIGATION	1575ed
20	Mobilization to Site	10d
21	Prepare Staging Area	1w
22	TASK 3: Site Investigation (Phase I)	134.38ed
23	Physical Characterization	116.38ed
24	Hydrogeologic Eval.	30d
25	Hydrologic Evaluation	5d
26	Soil/Sediment Evaluation	2d
27	Air Evaluation	1d
28	Human Population Evaluation	2w
29	Ecological Evaluation	4w

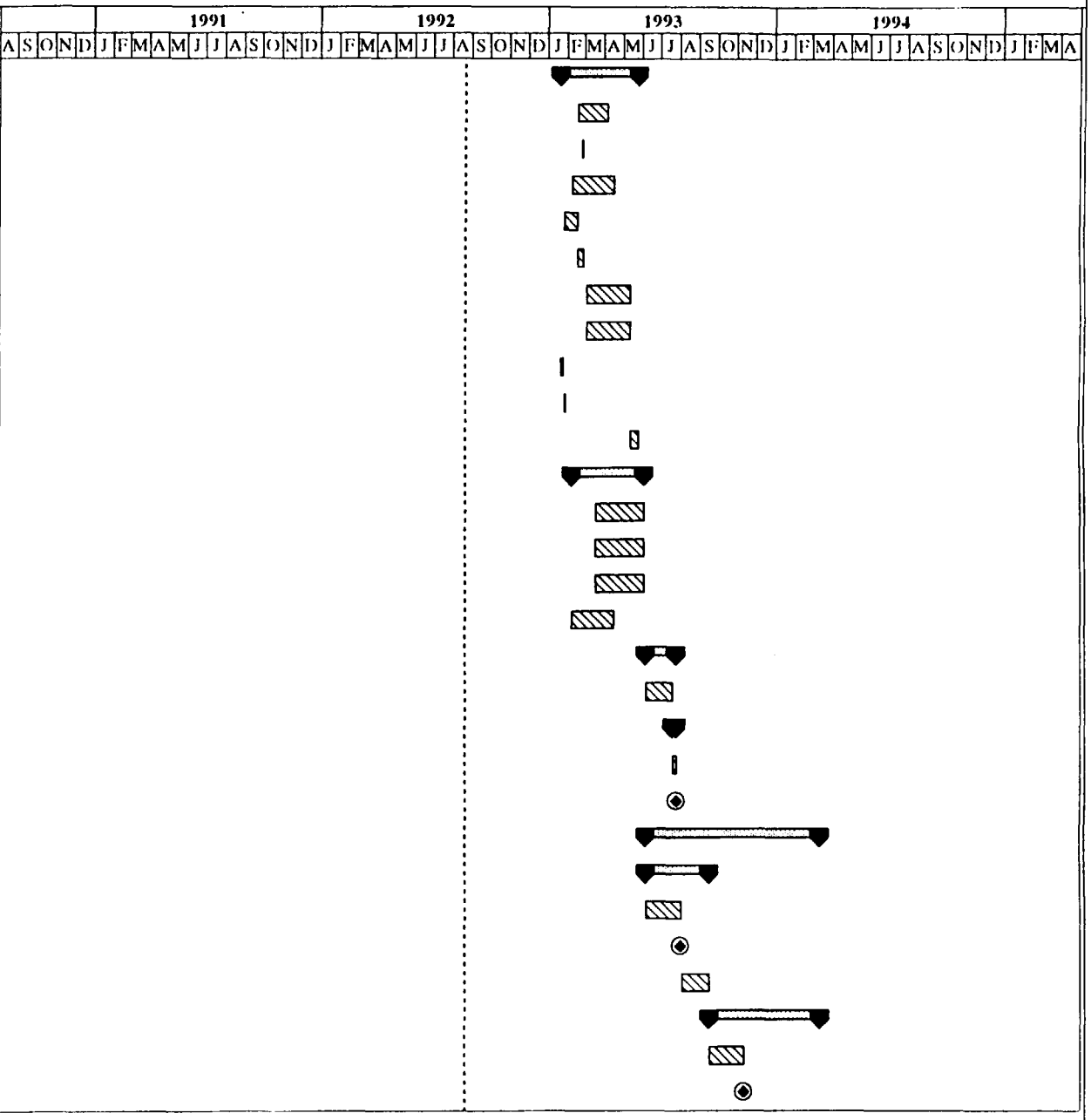
File Name:HOD5_92E.MPP
Date: 8/19/92
Page:1

Scheduled Activity **Milestone** **Summary**

d = work days ed = elapsed calendar days w = work weeks

FIGURE 1-2
H.O.D. LANDFILL RI/FS
ANTIOCH, ILLINOIS

ID	Name	Duration
30	Source Characterization	125.38ed
31	Cap Evaluation	34d
32	Leach Collect Sys. Eval	2d
33	On-Site Soil/Sed. Sampling/Analysis	10w
34	Leachate Piez./Gas Probes	16d
35	Downhole Gamma Logging	8d
36	Landfill Gas Sampling/Analysis	10w
37	Leachate Sampling/Analysis	10w
38	Landfill Borings	3d
39	Construct Perimeter Borings	3d
40	Off-Site Source Evaluation	2w
41	Migration Path./Contaminant Char.	116.38ed
42	Groundwater Sampling/Analysis	11w
43	Private/Muni. Well Sampling/Analysis	11w
44	Surface Water Sampling/Analysis	11w
45	Soil/Sediment Sampling/Analysis	10w
46	TASK 4: Site Investigation Analysis	49.38ed
47	Perform Site Invest. Analysis	6w
48	Tech Memo #1	6.38ed
49	Prepare Memo	1w
50	Tech Memo #1 to EPA	0d
51	TASK 5: Baseline Risk Assessment	278ed
52	Tech Memo #2 (BRA - TWP)	102ed
53	Prepare BRA -TWP	40d
54	BRA - TWP to EPA	0d
55	EPA Review / Comment	45ed
56	Baseline Risk Assessment	176ed
57	Prepare Draft BRA Report	8w
58	Draft BRA Report to EPA	0d



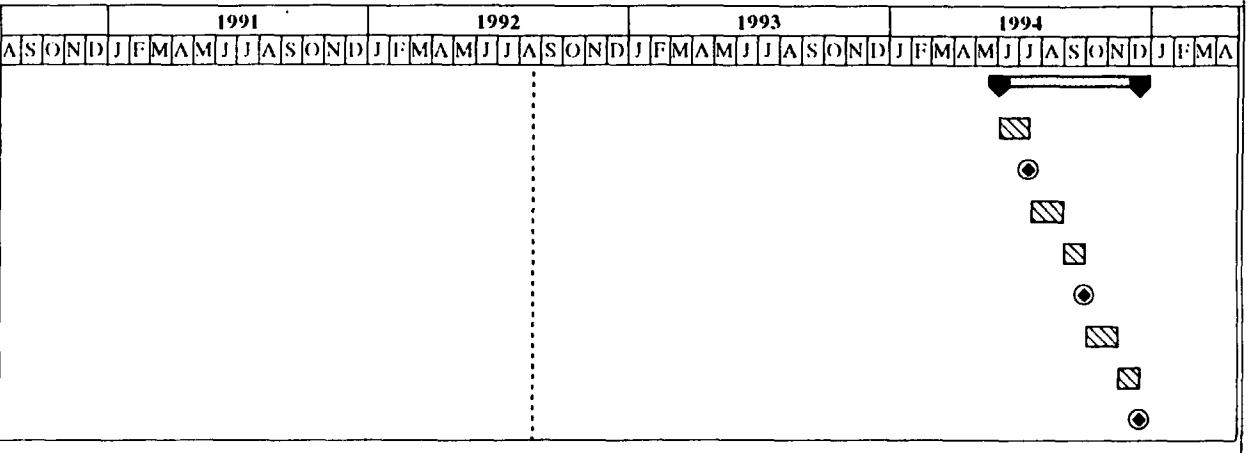
File Name:HOD5_92E.MPP
Date: 8/19/92
Page:2

Scheduled Activity **Milestone** **Summary**

d = work days ed = elapsed calendar days w = work weeks

FIGURE 1-2
H.O.D. LANDFILL RI/FS
ANTIOCH, ILLINOIS

ID	Name	Duration
88	TASK 14: FS Reports	197ed
89	Prepare Draft FS Report	6w
90	Draft FS Report to EPA	0d
91	EPA Review/Comment	45ed
92	Revise FS Report	30ed
93	Final Draft FS Report to EPA	0d
94	EPA Review FS Report	45ed
95	Revise FS Report	30ed
96	EPA Approval	0d



File Name:HOD5_92E.MPP
Date: 8/19/92
Page:4

Scheduled Activity **Milestone** **Summary**

d = work days ed = elapsed calendar days w = work weeks

WARZYN

Project Organization
H.O.D. Landfill RI/FS

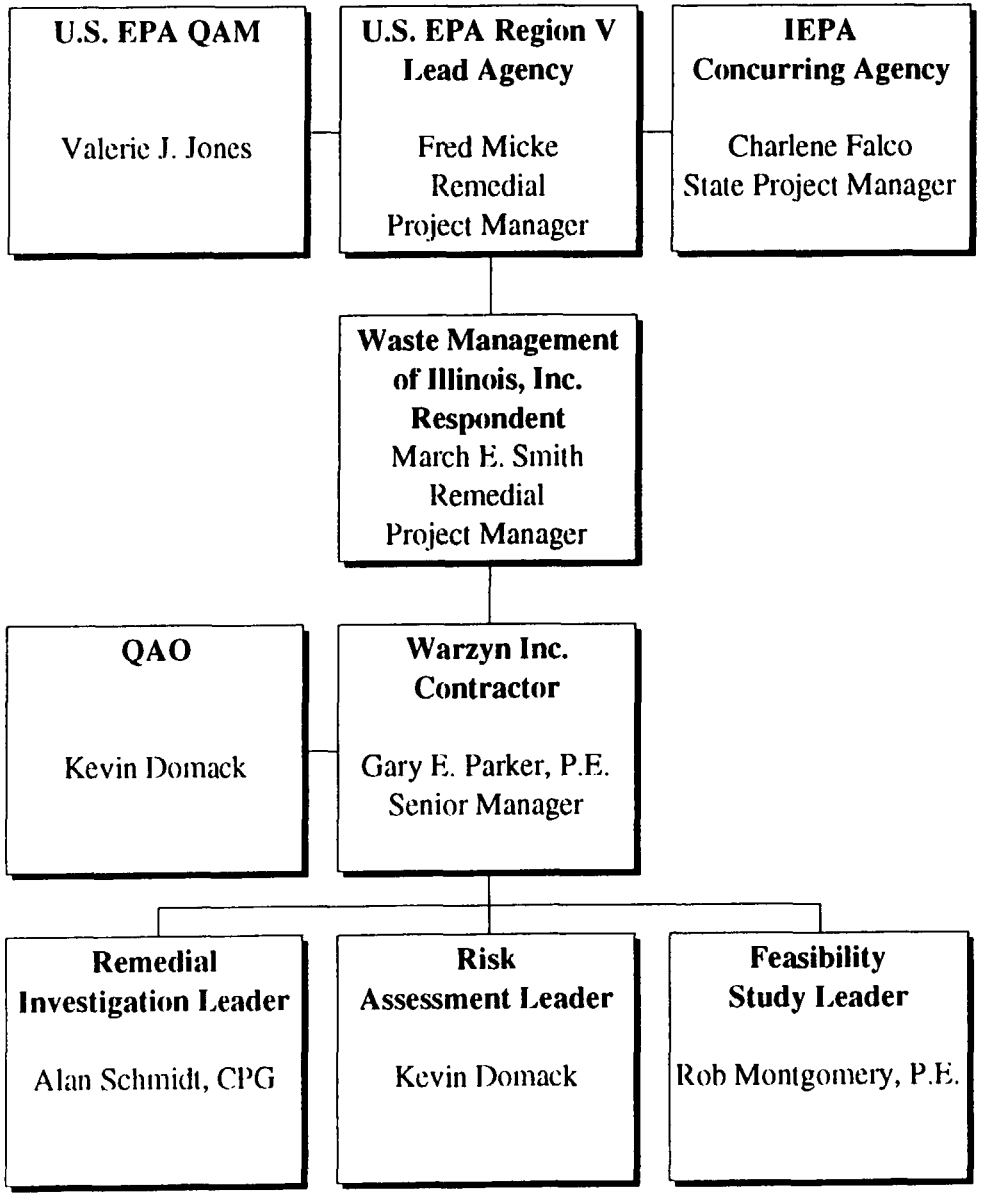


FIGURE 2-1

APPENDIX A

SAMPLING AND ANALYSIS PLAN (SAP)

TABLE OF CONTENTS

6

7

8

1

OBJECTIVES

The primary objective of the activities described in the Sampling and Analysis Plan (SAP) is to obtain representative data to be used for the Remedial Investigation/Feasibility Study (RI/FS) Analysis. Sampling activities described in this plan will be performed to complete the site investigation activities of the RI. Documentation procedures are described in the Data Management Plan.

The RI will consist of physical characterization, source characterization, and contaminant characterization. Data use objectives of the physical characterization include:

- Confirmation of the site stratigraphy, hydrogeology, hydrology, and ecology

Data use objectives of the source characterization site investigation include:

- Location and extent of contaminant source areas
- Investigation of chemical and physical characteristics

Data use objectives for the contaminant characterization include:

- Determination of potential migration pathways
- Evaluation of the magnitude and extent of groundwater contamination
- Evaluation of soil, surface water, sediment and air contamination

2

SCOPE

This Sampling and Analysis Plan (SAP) describes the procedures and practices (Section 5) to be used in obtaining site investigation data for use in the RI/FS. This plan also includes a description of sampling locations and number of samples (Section 3), the sample designation system (Section 4), decontamination and investigative waste disposal procedures (Section 6), and sample handling (Section 7) and sample documentation (Section 8) methods to be employed. The field activities, discussed in this report, include:

- Physical characterization
  - soil borings/soil sampling

- Source characterization
  - landfill cap evaluation
  - leachate collection system effectiveness (no sampling involved)
  - on-site surficial soil and sediment sampling
  - leachate piezometer installation (no sampling involved)
  - landfill gas probe installation
  - downhole gamma logging (no sampling involved)
  - leachate sampling
  - landfill gas sampling
  - landfill borings

- Contaminant characterization
  - groundwater sampling
  - private and municipal well sampling
  - surface water sampling

3

SAMPLING LOCATIONS AND NUMBER OF SAMPLES

3.1 PHYSICAL CHARACTERIZATION

The physical investigation will consist of a hydrogeologic evaluation designed to evaluate glacial stratigraphy around the perimeter of the Site. The evaluation will be accomplished by drilling eight soil borings around the perimeter of the Site through native unconsolidated deposits. The locations of the borings are specified in Table 8 and Drawing 60953-F10, both included in Volume 1 of 3 of the Work Plan.

Up to 16 soil samples, and 2 field duplicates will be analyzed for grain size.

3.2 SOURCE CHARACTERIZATION

Source characterization sampling and analysis activities will include landfill cap evaluation, on-site surface soil and sediment sampling, leachate sampling, landfill gas probe installation and landfill gas sampling, and landfill borings.

3.2.1 Landfill Cap Evaluation

Approximately 10 test pits will be performed to aid in evaluating the effectiveness of the existing cap to minimize infiltration of precipitation. Ten soil samples and one field duplicate will be collected and analyzed for grain size, Atterberg limits, natural moisture content, in-place density, and clay mineralogy using x-ray diffraction.

Test pits will be excavated using a backhoe. Field observations including density and nature of cover vegetation, root penetration, and evidence of inhomogeneities

in the cap will be recorded in a field notebook. Test pit profiles will be recorded on test pit logs.

3.2.2 On-Site Surface Soil and Sediment Sampling

On-site surficial soil and sediments will be collected in likely deposition areas in order to characterize contaminants. One sample from each of five areas of deposition (determined during site inspections) will be collected and analyzed for TCL organics, TAL inorganics, total organic carbon (TOC), grain size, natural moisture content, and Atterberg limits. One duplicate sample will also be collected and analyzed for the same parameters.

One soil sample will also be collected as matrix spike/matrix spike duplicate (MS/MSD) samples.

3.2.3 Landfill Gas Probe Installation

In order to assess methane gas production within the landfill, multi-stage landfill gas probes will be installed in the same boreholes as each new leachate piezometer. A total of thirteen new multi-stage gas probes will be installed. In addition, five perimeter gas probes will be installed on-site outside of the landfill area. Landfill gas monitoring will consist of monitoring percent methane, oxygen, carbon dioxide, and VOCs.

3.2.4 Leachate Sampling

In order to chemically characterize the leachate composition, samples will be collected from the following five locations: Manhole MHE and leachate piezometers LP1, LP6, LP8 and LP11. One duplicate sample, one field blank, and one MS/MSD will also be collected and analyzed.

Samples collected will be analyzed in the laboratory for TCL organics, TAL inorganics, chloride, sulfate, alkalinity, total hardness, nitrate nitrogen, nitrite nitrogen, ammonia nitrogen, TOC, and total dissolved solids (TDS). Field analysis will be conducted on each sample to determine field pH, field specific conductance, temperature, redox, and dissolved oxygen.

3.2.5 Landfill Gas Sampling

Approximately five landfill gas samples will be collected from landfill gas probes associated with leachate piezometers and/or gas well flares. Landfill gas samples will be collected at the following leachate piezometers: LP1, LP6, LP7, LP8, and LP11. Samples will be analyzed in the field for methane, oxygen, and carbon dioxide. Five investigative samples, one field blank and one duplicate collected will be submitted for VOC analysis.

3.2.6 Landfill Borings

In order to determine subsurface conditions and evaluate the feasibility of constructing a leachate barrier along the perimeter of the "old" landfill, approximately five soil borings will be drilled along the southern perimeter of the "old" landfill. Approximately ten soil samples (two from each boring) and one field duplicate will be submitted for grain size analysis.

3.3 CONTAMINANT CHARACTERIZATION

Contaminant characterization activities will include groundwater monitoring (water level measurements, in-situ hydraulic conductivity tests, new well installation, and sampling of new and existing wells), municipal and private well monitoring, and a hydrogeologic evaluation/surface water sampling.

3.3.1 Groundwater Monitoring

Eight monitoring wells will be installed at eight different locations around the site.

Initially, water level measurements will be made at all monitoring wells. Single well in-situ hydraulic conductivity tests will be conducted at selected existing and new monitoring wells (see Work Plan Section 4.4.2). Prior to new monitoring well installation, existing monitoring wells will be inspected to confirm that each is functional and capable of being sampled.

Phase 1 groundwater sampling will consist of sampling the following wells and analyzing for TCL/TAL parameters, alkalinity, chloride, hardness, sulfate, TOC, total dissolved solids (TDS), nitrate nitrogen, nitrite nitrogen, and ammonia nitrogen:

- US1S and 1D
- US4S and 4D
- US6S, 6I and 6D
- G11S and 11D
- W5S
- US3S, 3I, and 3D
- W4S
- W6S
- W7D

3.3.2 Municipal/Private Well Monitoring

Municipal wells 3 and 5 and up to six private groundwater supply wells will be sampled and analyzed for for TCL organics and TAL inorganics. One field duplicate and field blank will be collected for each analysis. An MS/MSD sample will also be collected and analyzed for TCL organics. Private well sampling will be coordinated with the Lake County Health Department. Field parameters will consist of pH, conductivity and temperature.

3.3.3 Surface Water Sampling

Three surface water samples will be collected for analysis of TCL organics and TAL inorganics. One field duplicate and field blank will be collected for each analysis. An MS/MSD sample will also be collected for TCL organic analysis. Field parameters will consist of pH, conductivity, temperature, redox, and dissolved oxygen.

During sampling, surface water levels and flow rates will be measured. A physical inspection of the Sequoit Creek banks will also be conducted.

3.4 QUALITY ASSURANCE SAMPLING

Quality control samples will collected during sampling activities associated with the physical characterization of soils, and the chemical characterization of sediments/surface soils, leachate, landfill gas, groundwater and surface water. Quality control samples will consist of sample duplicates, field blanks and matrix spike/matrix spike duplicate (MS/MSD) samples as described below.

3.4.1 Field Blanks

For sediment and soil samples, no field blanks will be collected due to the unavailability of suitable blank material. For water and leachate samples, one field blank will be prepared for each type and container size. Field blanks will be prepared according to the following schedule for each sampling activity:

- One field blank for every 10 or fewer samples collected; and
- For each sampling period, a minimum of one blank for each group of parameters per sample matrix.

The field blank samples will be prepared using deionized water stored in polyethylene containers. The water will be routed through the appropriate sampling equipment following decontamination. Landfill gas field blanks will be prepared by collecting a sample of ambient air after decontamination of the sampling system.

3.4.2 Matrix Spike and Matrix Spike Duplicates (MS/MSD)

For water and leachate samples, one sample per group of 20 or fewer samples collected for VOA and extracted organics analysis during each sampling activity will be selected for MS/MSD analysis. MS/MSD samples will not be collected for inorganic analysis.

For soil samples, two MS/MSD samples will be collected for organic analysis.

3.4.3 Sample Duplicate

One duplicate sample will be collected for each increment of 10 or fewer samples collected for each matrix during each sampling period. A duplicate sample will consist of a sample obtained from the same sampling device as the original sample.

3.4.4 Trip Blanks (TB)

A trip blank for VOC analysis will be included in each sample shipment containing water matrix samples for VOCs. The trip blank will consist of two 40-ml VOC vials filled with deionized water with a Milli-Q cleanup. It will be prepared in the laboratory or office, transported to the field and shipped with the other samples to the designated laboratory without being opened. It will be packaged using standard procedures as for the other sample bottles.

4

SAMPLE DESIGNATION

A sample numbering system will be used to identify each investigative and quality control sample. Each sample identifier will include the project identifier code, sample type and location code, and a sampling event code. The sampler will maintain a log book containing the sample identification listings.

4.1. PROJECT IDENTIFIER CODE

A two-letter designation will be implemented to identify the sampling site. The project identifier will be "HD" to signify the HOD Landfill Site in Antioch, Illinois.

4.2. SAMPLE TYPE AND LOCATION CODE

Each sample collected will be identified by a two-letter code corresponding to the sample type. Sample type codes to be used for the subtasks covered in this sampling plan include:

- GW - groundwater sample from monitoring well
- SS - split spoon or soil boring sample
- SD - sediment sample
- SW - surface water sample
- SU - surface soil sample
- PW - groundwater from a private residential well or municipal well
- SC - soil sample collected from test pits of the clay cap
- LC - leachate sample
- LG - landfill gas
- FB - field blank
- TB - trip blank

Other letter designators may be added for sample activities of later subtasks.

The location code will follow the sample type code. The location code consists of a two-to-five digit numeric or alpha-numeric code that indicates the sample location. Surface water, sediment, field blanks, and air samples will use a consecutive numbering system starting at 01, assigned in the field.

4.3. SAMPLING ROUND CODE/DUPLICATE CODE

A two-digit numerical code will be used to designate additional location information. For soil samples, the Round code will represent the depth of the sample in feet below the ground surface. Duplicate samples will be designated by the Round code preceded by a 9. Matrix spike and matrix spike duplicate samples are collected as additional sample volume at selected locations.

Although identified as such on chain-of-custody records, specific sampling codes will not be provided for matrix spike or matrix spike duplicate samples.

4.4 EXAMPLES OF SAMPLE NUMBERS

Examples of sample number codes are as follows:

- HD-SSW5S-15 = HOD Landfill, split spoon sample from monitoring well W5S at a depth of 15 feet.
- HD-SCTP7-3 = HOD Landfill, soil sample of clay cap collected from at Test Pit 7 a depth of 3 feet.

5

GENERAL SAMPLING EQUIPMENT AND PROCEDURES

5.1 SOIL BORINGS AND SOIL SAMPLING

5.1.1 Objective

The objective of this activity is to physically characterize the subsurface soils and to confirm the local glacial stratigraphy.

5.1.2 Personnel and Responsibilities

A drill crew of two individuals will perform the borings for soil samples. A geologist will supervise their efforts, collect soil samples and function as site safety officer.

5.1.3 Methods

Borings will be drilled using 4.25-inch inner diameter (ID) x 8.5-inch outer diameter (OD) or 6.25-inch ID x 10.25-inch OD hollow stem augers. Soil samples will be collected with split spoon samplers, visually classified in the field by a geologist and placed into the appropriate sampling jars. Soil samples will be collected at 2.5 foot intervals. Selected soil samples will be analyzed in the laboratory for grain size. Two samples will be collected from each boring for analysis.

Soil samples will be selected for analysis based on visual observations, sample depth and stratigraphy.

5.2 LANDFILL CAP EVALUATION

5.2.1 Objective

The objective of this activity is to evaluate the effectiveness of the existing cap.

5.2.2 Personnel and Responsibilities

Test pits will be excavated by a crew of two individuals, one individual will operate the backhoe under the supervision of a geologist. The geologist will observe the excavation and record observations and function as the site safety officer.

5.2.3 Methods

At each test pit location, topsoil will be carefully scraped away and placed to one side. Cap materials will then be excavated and placed separately from the covered materials. The on-site geologist will observe and describe and photodocument the excavation. Excavations will be terminated at approximately 5 to 6 feet or when the on-site geologist and U.S. EPA oversight professionals agree that the cap profile has been adequately evaluated.

Air monitoring for health and safety purposes will be conducted with a photoionization detector (PID).

Decontamination will include steam cleaning the backhoe bucket before the initial excavation during each visit and between subsequent excavations to minimize carry-over contamination.

5.3 SURFICIAL SOIL AND SEDIMENT SAMPLING

5.3.1 Objective

The objective of this activity is to chemically characterize site surficial soils/sediments.

5.3.2 Personnel and Responsibilities

A crew of two individuals will collect samples.

5.3.3 Methods

Samples will be collected using a stainless steel trowel and will be transferred directly to the appropriate sample jars. Samples will be analyzed in the laboratory for U.S. EPA CLP TCL and TAL parameters, and physical parameters (TOC, grain size, natural moisture content, and Atterberg limits).

5.4 LANDFILL GAS MONITORING

5.4.1 Objective

The primary objective of this activity is to monitor the presence of landfill gas (LG) within and outside the landfill and, if found, conduct analysis to determine percent methane, oxygen, and carbon dioxide, and the presence and concentrations of volatile organic compounds (VOCs).

5.4.2 Personnel and Responsibilities

A geologist, hydrogeologist, or field engineer, and a technician, will be responsible for obtaining landfill gas samples.

5.4.3 Methods

Samples of landfill gas will be collected for VOC analysis in the following manner:

- Samples will be collected in canisters provided by the analytical laboratory. Each canister is under vacuum, and has a valve opening.
- One end of tygon tubing will be attached to the canister; the other end will be attached to the gas probe that has been purged using a personal sampling pump.
- The absolute pressure of the cannister is recorded and the valve connecting the canister to the tubing will be opened for two minutes, allowing the sample to collect in the canister.
- The valve will then be closed, and the tygon tubing disconnected and the absolute measure again recorded.
- The canister will be stored in a cooler for shipment to the laboratory.
- Appropriate field information will be included in the cannister sampling field data sheet shipped with each canister.

Percent methane, oxygen, and carbon dioxide will be measured in the field using a GasTech or similar monitoring instrument.

5.5 LEACHATE SAMPLING

5.5.1 Objective

The primary objective of this activity is to chemically characterize leachate.

5.5.2 Personnel and Responsibilities

A team of two individuals will be responsible for the sampling.

5.5.3 Methods

Each leachate piezometer will be sampled using a stainless steel bailer attached to stainless steel cable. The sampling equipment will be cleaned between wells with a Liquinox or other non-phosphate detergent solution and will be rinsed with deionized water.

Decontamination will include steam cleaning or high pressure hot water washing the drilling equipment and tools between field boreholes and detergent washing and water rinsing the split-spoon samplers after each collected sample. Decontamination fluids and borehole cuttings will be containerized and stored in a secure area pending results of groundwater and soil analyses. If borehole cuttings, purge water, decontamination water are found to be contaminated, these materials will be disposed of appropriately after consultation with EPA.

5.6 MONITORING WELL INSTALLATION AND ASSOCIATED TESTING

5.6.1 Objective

The objective of this activity is to determine groundwater flow direction and physical characteristics of the geologic media in the site area.

5.6.2 Personnel and Responsibilities

Groundwater monitoring wells will be installed and soil borings performed by a drill crew of two individuals each. Monitoring well installation and soil borings will be supervised by a geologist, who will collect soil samples and function as the site safety officer. Water levels will be measured by a technician. Hydraulic conductivity tests will be performed by a team of two individuals.

5.6.3 Methods

Monitoring Well Installation - Each boring will be drilled using 4.25-inch ID or 6.25-inch ID hollow stem augers from ground surface to the base of the boring. Soil samples will be collected at ground surface and at 2.5 ft intervals to the base of the boring. Split-spoon samples will be analyzed for grain size and Atterberg limits (if appropriate). The purpose of these analyses is to confirm field

identification of soils and to assist in assessing subsurface soils as a contaminant migration pathway. Soil samples will be field screened with a PID to assess potential hazards to the field personnel.

Final soil boring logs will be prepared based on field observations, soil testing, and laboratory sample classification. Soil samples and rock cores will be retained by Warzyn for the respondents until termination of the RI/FS. Procedures for sample handling are discussed in the QAPP.

Monitoring wells will be constructed of 2-inch ID Schedule 40 PVC pipe. Water table wells will be constructed with 10-ft long, PVC screens placed so the screen is likely to intercept the water table. Piezometers will be constructed with 5 ft long PVC screens.

The annular space between the well and the edge of the borehole will be backfilled with clean silica sand to approximately 2 ft above the top of the well screen. At water table wells, the remainder of the annulus will be backfilled with granular bentonite. At piezometers, a fine silica sand or bentonite pellets will be placed above the filter pack and bentonite slurry placed above the fine silica sand or bentonite pellets. The remainder of the annular space will be backfilled with a sodium based bentonite slurry. Where more than 5 ft of slurry needs to be placed, a tremie pipe will be used. A locking steel protective casing will be installed at the surface of each well.

A PID will be used to monitor air quality for site safety purposes and to screen soils for VOCs. Drill cuttings from the boreholes will be containerized if PID readings exceed 5 ppm. Water used during the drilling operations and well development will be containerized pending results of groundwater sample analysis.

To minimize potential inadvertent contamination by drilling equipment and/or inter-borehole contamination, steam cleaning will be used. The drill rig and drilling tools will be steamed cleaned before mobilization onto the site. The drilling tools coming into contact with site soils will be steam-cleaned between each boring. Water from the steam cleaning will not be collected.

The split-spoon sampler will be cleaned in a liquinox or non-phosphate detergent solution between samples. Water from split-spoon cleaning will not be collected. Well pipe, screen and protective casings will be steam cleaned or washed with a high pressure hot water washer before installation. Water from steam cleaning will not be collected.

New monitoring wells will be developed by alternatively surging and purging each wells using a bailer for a minimum of 30 min. After the surge and purge cycles are completed, the well will be pumped until 10 well volumes are removed or until the well produces sediment free water. Purged water will not be collected.

Water Level Measurements - Water levels in existing and new monitoring wells will be measured. An electronic water level indicator will be lowered into the observation wells until the water level is reached. Depths will be recorded to the nearest 0.1 ft.

In-Situ Hydraulic Conductivity Tests - Hydraulic conductivity will be measured by drawdown testing in selected shallow water table wells and by air pressure in deeper piezometers. Hydraulic conductivity testing will be conducted after groundwater quality sampling. The methods to be used are as follows:

- Measure water level with a tape and sounding device or electronic water level indicator.
- Place the pressure transducer into the well and allow approximately three minutes for the probe to equilibrate to the water temperature and pressure.
- Install the well head device to seal the well head (for piezometers only).
- Enter the reference water level into the data logger and check the water level using the pressure transducer until water level reading is stable.
- After a stabilized water level reading is obtained from the pressure transducer, the well is pressurized with sufficient air pressure to displace 10 ft of water (0.4 PSI/ft of water) (for piezometers only).
- Air pressure is maintained until the water level reading from the transducer is constant (for piezometers only).
- The air pressure is then instantaneously released while running the pressure transducer recorder in the log sampling mode (for piezometers only).
- At water table wells a single bailer full is removed to reduce the water level, while running the pressure transducer recorder in the log sampling mode.
- The test results are immediately printed out to obtain a hard copy.

- Data are transferred to a micro-computer.

5.7 GROUNDWATER QUALITY SAMPLING

5.7.1 Objectives

The objective of groundwater sampling is to determine the nature, magnitude and extent of groundwater contamination.

5.7.2 Personnel and Responsibilities

A crew of two technicians will collect samples.

5.7.3 Methods

New and selected existing monitoring wells will be sampled during the investigation. Sampling will not be conducted for a minimum of two weeks after well development. Several private wells and municipal wells may also be sampled during the investigation. Groundwater sampling will proceed from wells expected to have the lowest contaminant concentrations (based upon observations during drilling and existing groundwater quality data), to the wells suspected of having the highest contaminant concentrations. Each sampled well will be purged immediately prior to sampling using a submersible sampling pump, stainless steel bailer attached to stainless steel cable, or bladder pump. The volume of water removed from the well will be measured so that a minimum of three well volumes are removed. Groundwater samples will be collected immediately after well purging has been completed. Samples to be analyzed for VOCs will be collected first to minimize volatilization.

The sampling equipment and water level measurement tape will be cleaned between wells with a Liquinox or another non-phosphate detergent solution and rinsed with deionized water.

Groundwater sample blanks will be collected by pouring deionized water from the sampling device into the sample bottles. Matrix spike/matrix spike duplicate samples will be collected using the same device used for groundwater sample collection. Duplicate samples for volatile organics analysis will be obtained by alternately filling VOC vials for the primary and duplicate sample. The remainder of the sample for inorganic analysis, will be split between the principle sample and the duplicate sample.

5.8 SURFACE WATER CHARACTERIZATION

5.8.1 Objective

The objective of the surface water investigation is to chemically characterize surface water.

5.8.2 Personnel and Responsibilities

A team of two technicians will collect surface water samples and provide their own site safety monitoring.

5.8.3 Methods

VOC samples will be collected first to minimize volatilization. Samples for metal analysis will be unfiltered. Surface water samples will be collected using stainless steel dippers as sampling equipment. Sampling equipment will be decontaminated using Liquinox or another non-phosphate detergent and rinsed with deionized water.

5.9 PRIVATE/MUNICIPAL WELL SAMPLING

5.9.1 Objective

The objective of the private/municipal well sampling is to chemically characterize water quality in area drinking water supplies.

5.9.2 Personnel and Responsibilities

A team of two technicians will collect samples.

5.9.3 Methods

Prior to sampling, the water system will be purged. Sampling will be conducted at the tap closest to the source; screens, aerators, filters, etc. will be removed prior to sampling. Water flow will be adjusted to a smooth-flowing stream and samples collected directly in sample jars.

6

DECONTAMINATION AND INVESTIGATIVE WASTE DISPOSAL PROCEDURES

6.1 DECONTAMINATION PROCEDURES

Procedures to be followed to decontaminate equipment and personnel are described in the Site Health and Safety Plan. The procedures are summarized below.

Site Personnel Decontaminate Procedure:

- Dispose of outer latex booties
- Wash boots in Liquinox bootwash
- Clean outer gloves in Liquinox wash solution (discard if too soiled to clean thoroughly)
- Dispose of polycoated tyvek suits
- Dispose of surgical gloves
- Wash hands in hand wash
- Wash face and neck in face wash
- Clean and sanitize face mask

Site personnel will perform the above mentioned decontamination procedure at a specified decontamination area prior to leaving the site.

Discarded clothing and other articles will be collected in double-lined, heavy duty garbage bags.

Equipment and vehicle decontamination procedure:

- Decontamination will be performed prior to site entry
- Decontamination will be performed on-site
- Gross contamination will be removed with a brush and Liquinox solution
- Steam cleaning or hot water high pressure washing will follow

The drilling equipment and the backhoe will be steam cleaned or high pressure hot water washed, at a designated decontamination area, between boring/excavation locations and prior to exiting the site. The equipment and vehicle decontamination area will be constructed above grade adjacent to an existing on-site manhole. The catchment will be lined and will drain to the existing manhole. Collected waste water will be immediately pumped from the manhole into the temporary leachate tanker and disposed of with the extracted leachate. The equipment decontamination area will be located away from the designated personnel decontamination area.

Decontamination will include steam-cleaning or hot water high pressure washing the drilling equipment, backhoe and tools between boreholes and test pits, and detergent washing and water rinsing the split spoon samplers after each collected sample. The drill rig and equipment may also require scrubbing of accessible parts with a detergent/water solution. Well materials will also be steam-cleaned or hot water high pressure washed and wrapped in plastic until installed. The bailer cable, trowels, spatulas, stainless steel bucket and water level measurement tape will be cleaned with Liquinox or another non-phosphate detergent solution, and rinsed with deionized water.

Equipment remaining on-site overnight will be decontaminated at the end of the day, if not done earlier in the day.

6.2 INVESTIGATIVE WASTE DISPOSAL PROCEDURES

Performance of the remedial investigation will generate liquid and solid investigative wastes. The disposition of these wastes is described below.

6.2.1. Monitoring Well Fluids

Waste liquids derived from the development or purging for sampling of monitoring wells will be collected and disposed with leachate.

6.2.2. Soils

Impacted soil will be generated through drill cuttings in the performance of soil borings. These soils will be segregated on the basis of whether impacts are indicated by PID field screening. Soils are considered impacted if PID readings are greater than 10 ppm. Non-impacted soil (<10 ppm) will be left in the area near the soil boring. Impacted soils (>10 ppm) will be stored on-site in a covered roll-off container until a final site remedy is selected. When the final remedy is implemented, the impacted soils may be incorporated with the waste under the final remedy, or handled as a solid waste if they pass the TCLP test.

7

SAMPLE HANDLING AND ANALYSIS

7.1 PARAMETERS

Samples collected for chemical analysis will be analyzed by a laboratory approved by the U.S. EPA Region V Contract Program Management Section (CPMS). Chemical parameters for which groundwater and surface water may be analyzed are summarized below:

- U.S. EPA CLP TCL organics
- U.S. EPA CLP TAL inorganics
- Field pH
- Field Specific Conductance
- Chloride
- Sulfate
- Alkalinity
- Nitrate - Nitrogen
- Nitrite Nitrogen
- Ammonia - Nitrogen
- Total Organic Carbon
- Total Dissolved Solids

Measurement of pH, specific conductance and temperature, dissolved oxygen and redox will be performed in the field. The groundwater samples to be analyzed for inorganics (with the exception of cyanide) will be field filtered with 0.45 micron filters within 15 minutes of sample collection. Surface water and private/municipal well samples will not be field filtered. Surficial soil and sediment samples will be analyzed for U.S. EPA TCL and TAL parameters and grain size, Atterberg limits, TOC, and natural moisture content. Soil samples from monitoring well installation borings will be analyzed for grain size and Atterberg limits (if appropriate).

Soil samples from the landfill cap evaluation will be analyzed for grain size. Atterberg limits, natural moisture content, density, and clay mineralogy. Leachate samples will be analyzed for the same parameters as groundwater. Landfill gas samples will be analyzed for VOCs, methane, oxygen, and carbon dioxide.

7.2 SAMPLE PRESERVATION

Samples will be collected and preserved in a manner appropriate for the analyses they receive (see Table 1-2 of the QAPP). The portion of groundwater samples requiring field filtering prior to analysis (see Table 1-2 of the QAPP) will be filtered using a pressure filtration device, through a 0.45 micron filter, as soon as possible after collection. Filtered portions of the samples will be preserved, as appropriate, immediately after filtration. Sample fractions will be preserved before shipment according to the procedures shown in Table 1-2 of the QAPP. Preservatives added to the samples will be prepared using reagent grade chemicals. Table 1-2 of the QAPP should be consulted for details regarding sample packaging and shipping.

8

SAMPLE DOCUMENTATION

Field sampling activities will be documented using a bound notebook/logbook. Information recorded in the field notebook will include date of sampling, sampler, weather conditions, observations and methods of preservation. Additional data pertaining to sampling may also be included in the logbook. Landfill gas samples collected in stainless steel canisters will be documented on canister sampling data sheets.

Samples will be collected under chain-of-custody procedures. Standard forms including sample labels, sample tags, chain-of-custody forms, and custody seals used for sample tracking will be maintained (see attachments). A brief description of sample documents follow:

A. Chain of Custody Form

1. One Form per shipping container (cooler).

2. Carrier service does not need to sign form, if custody seals remain intact.

3. Use for all samples

B. Chain of Custody Seals

1. Two seals per shipping container to secure the lid and provide evidence that samples have not been tampered with.

2. Cover seals with clear tape.

3. Record seal numbers on Chain of Custody Form.

4. Use for all samples.

C. Sample Tags

1. Each sample container must have a sample tag affixed to it.

2. Sample tag numbers are recorded on the Chain of Custody Forms.

3. Use for all samples.

D. Sample Identification Record Form will:

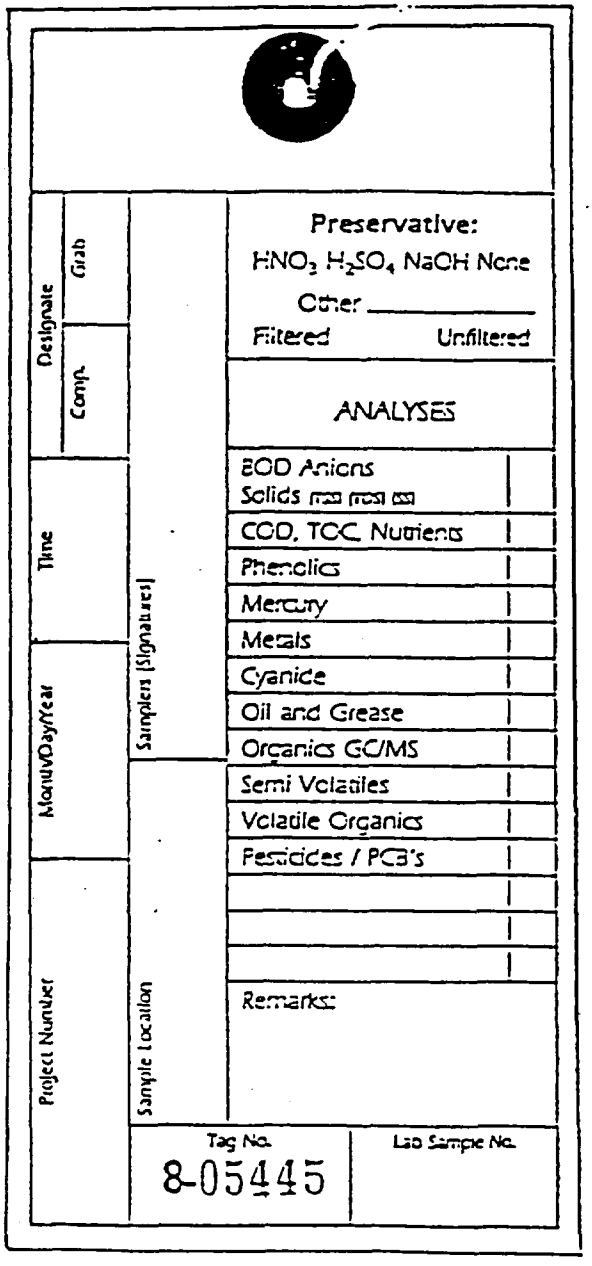
1. Provide means of recording crucial sample shipping and tracking information.

2. Contain information such as:

- Sample number
- Sample matrix
- Sample location code
- Sample round
- Chain of custody number
- Lab code
- Date sampled
- Date shipped
- Airbill number
- Sampling tag number

Paperwork accompanying the samples being shipped to the laboratory will be sealed in a plastic bag that is taped to the inside of the cooler lid. Copies of the chain-of-custody forms, and other paperwork (if possible), will be retained with the field files.

Two sample seals will be placed on opposite sides of the lid and extending down the sides of the cooler. The lid will be securely taped shut prior to shipment.



SAMPLE TAG

Project # _____ Lab # _____

Sample Description _____

Date Collected _____ By _____

Preservative: HNO_3 H_2SO_4 NaOH None Other ____

Filtered Unfiltered

SAMPLE LABEL

FIGURE 1

Sample Custodian Signature: _____

Date: _____

(Circle Appropriate Response)

Custody Seal — present/absent; intact/not intact

Chain-of-Custody — present/absent

Sample Tags; Sample Tag Numbers — present/absent; listed/not listed on chain-of-custody

Project Number: _____

Airbill Number: _____

Date Rec'd	Time Rec'd	Chain-of Custody Record No.	Corresponding Sample Tag Nos.	Corresponding Assigned Nos.	pH <2	pH >9	pH >12	Does info. on Custody Records, Traffic and Sample Tags Agree	Remarks Condition of Samples

Chain of Custody Seal

APPENDIX B

ANALYTICAL SERVICES
STANDARD OPERATING PROCEDURES (SOPs)

APPENDIX B-1

ALKALINITY (WARZYN)

Effective: 5-23-91

ALKALINITY - AUTOANALYZER

Scope and Application: This method is applicable to drinking water, surface water, groundwater and wastewater.

Reference: EPA 1983, Method 310.2 Lachat Instruments 1988, Method 10-303-31-1-A

Sample Handling: Refrigerate at 4°C and analyze within 14 days of collection.

Detection Limit: 10 mg/L as $CaCO_3$

Optimum Range: 10 - 500 mg/L

Instrument Conditions:

1. Pump speed: 35
2. Cycle period: 40 seconds
3. Load period: 25 seconds
4. Inject period: 15 seconds
5. Inject to start of peak period: 5 seconds
6. Inject to end of peak period: 44 seconds
7. Gain: 150 x 10
8. Zero: 180
9. Interference filter: 410 nm
10. Sample loop: 90 cm
11. Standards for curve set-up: 0, 20, 50, 100, 250, 500 mg/L.

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated.)

1. **Degassed Milli-Q water - 2 options:**

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.

   b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water (15 min/20 L.) Store in cubitainer.

2. **Stock alkalinity standard (1000 mg/L as $CaCO_3$):** In a 1 liter volumetric flask, dissolve 1.060 g of anhydrous primary standard grade sodium carbonate (Na_2CO_3-dried at 250°C for 4 hours) in approximately 900 mL of helium purged Milli-Q water, and dilute to mark.

3. **Standards:** (Prepare fresh every month). Dilute to volume using degassed Milli-Q water. Refrigerate.

Concentration of Standard	Letter Identifier	Volume of Alk. Stock	Dilute to
0 mg/L	A	0	200 mL
20 mg/L	B	4.0	200 mL
50 mg/L	C	10	200 mL
100 mg/L	D	50	500 mL
250 mg/L	E	125	500 mL
500 mg/L	F	100	200 mL
CRDL 10 mg/L		2.0	200 mL

Note: Final volumes are not the same! Computer refers to standards by letter.

4. **Hydrochloric acid (0.1M):** In a 1 liter flask, dilute 8.3 mL of concentrated HCL in D.I. water and dilute to the mark.

5. **KHP buffer (0.025 M, pH 3.1):** In a 1 liter flask, dissolve 5.10 g of primary standard grade potassium acid phthalate (KHP) ($KHC_8H_4O_4$) in approximately 800 mL of Milli-Q water. Add 70 mL of 0.1M HCl, then carefully, add additional acid to bring pH to between 3.10 and 3.12. **Note:** Use only 0.1M HCL to adjust the pH of buffer. Do **not** back adjust the pH with NaOH. Vacuum filter through a 0.45 micron membrane filter. **Store In Glass and Prepare Daily!**

6. **Methyl orange reagent:** In a 1 liter volumetric flask, dissolve 0.125 g of methyl orange indicator in about 700 mL of Milli-Q water and dilute to the mark. **Mix well and vacuum filter through a 0.45 micron membrane filter before each use.** Store in amber glass! **Note:** Amount of methyl orange may be adjusted to correct for variances in lots of methyl orange.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum working range.

2. The gain and zero settings are guidelines and must be optimized each day.

3. The alkalinity standards can be combined with chloride and sulfate standards for use with the 3 channel method.

4. Turbidity will interfere. Samples must be filtered prior to analysis. (Use Whatman #1 or #4 filter paper.)

5. Color will interfere, dilute the sample and also spike the dilution to confirm the quality of the result.

System Operation:

1. Refer to "Auto Analyzer Operation start-up procedure." (IOP# LAAC-Section A).

2. Analyze an initial calibration check standard, a blank, a CRDL standard and a known reference standard at the beginning of each run. The blank must be below the detection limit and the standards must be within required control limits before any samples are analyzed.

3. Spike samples by mixing sample with an equal volume of 250 mg/L standard (E), for a final spike level of 125 mg/L.

4. The calibration check standard is 100 mg/L (D).

5. Refer to "Auto Analyzer shut-down procedure". (IOP# LAAC-Section B).

Quality Control:

1. Establish a standard curve with the standards listed above. The derived concentration of each calibration must be $\pm$ 10% of the true value. The derived value for the blank must be below the method detection limit.

2. The CRDL standard concentration should be at the method detection limit (MDL). Results must be within the acceptable limits of ± the MDL or the instrument must be re-calibrated before samples are analyzed.

3. A quality control calibration check standard of 100 mg/L (D) and a blank are to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration check standard and blank are still required. The last samples analyzed in the run are to be the calibration check standard and blank. Standards must be within the acceptable ranges and blanks must be below the method detection limit or the samples run after the last acceptable calibration check standard and blank are to be reanalyzed.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicates are to be within acceptable ranges or data must be flagged appropriately.

Calculation:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer. See LAAC SOP for further detail.

AUTOANALYZER

Scope and Application: Ions can be readily analyzed by a flow-injection autoanalyzer. The flow injection design gives the system excellent washout characteristics, to prevent carry over and cross contamination. The autoanalyzer is generally more sensitive and accurate than the manual wet-chemistry techniques.

Method: Flow injection

References: Lachat Instruments, 1986.

Sample Handling: See separate SOP's for requirements.

Reagents and Apparatus:

1. Lachat 3-channel autoanalyzer
2. Stock and standard ion solutions
3. Class A volumetric flasks
4. Class A volumetric pipets
5. Milli-Q water
6. Required interference filters
7. Disposable 4 mL cups
8. Automatic sampler
9. Proportioning pump
10. Injection module
11. Colorimeters
12. Manifolds
13. Columns - if needed
14. Helium gas
15. Computer
16. Printer

Procedure:

A. Instrument Set-Up

1. Depress red power switch on power strip located behind the computer terminal. This will turn on the computer, the screen, and the printer.

2. Depress red power switch on rear power strip on Lachat system.

3. Select manifold and make appropriate hydraulic connections.

   Hydraulic connections:

a. Use correct sample loop length to connect. Lines 1, 4.

b. Line 2 is carrier line.

c. Line 3 goes to manifold.

d. Line 5 goes to waste container.

e. Line 6 comes from sample probe.

f. Connect manifold to flow through cell.

Tension levers should be up when pump tubing is inserted. Snap pump tubing cartridges into place.

4. Insert correct filter.

5. Pump Milli-Q water through lines for 5 minutes by depressing the pump ON button. Check for leaks.

6. Computer - At the C> type in "quikcalc". This calls up the Lachat software and puts you at the master menu. Press <enter>.

7. Put lines into reagents and/or degassed Milli-Q water.

8. Computer - Select "Load/Stop Background Method" on the master menu. Press <enter>.

9. Select appropriate method. Press <enter>.

10. Printer should be set at FONT 0.

11. Pump reagents until a steady baseline is achieved.

12. When using a method with a column (SO_4 or NO_3), the column may be inserted at this point. See method SOP's for more details.

13. For each analytical channel, adjust zero knob so that the baseline is near the bottom of the screen (between .000 - .030).

14. Adjust gain while injecting top standard.

    a. Place autosampler probe into the highest standard bottle.

    b. After 20-30 seconds, press cycle button on front panel so that LED light is red. This is the load position.

    c. After 25 seconds (or less depending on sample loop size), press cycle button so that LED light is green. This is the inject position.

d. Adjust gain knob on detector so that peak reading on the colorimetric is 1.700-1.950.

e. Repeat until gain is properly adjusted.

f. Wipe probe and replace the autosampler probe into the sampler.

15. Select menu item by going into foreground. (Press and hold Alt key, then press Esc key).

    a. Select "Sample Tray Information and Start Analysis" on master menu. Press <enter>.

    b. Press <enter> or type in sample tray reference number if it is a tray which has already been typed in.

    c. Enter tray ID and operator. Check "Display Standards Position in Tray" to insure the tray is set-up properly.

    d. Select "Enter Sample ID's". Press <enter>.

    e. Type in sample information. Check standards will automatically be placed in the tray information portion.

    f. Press Esc once to return to menu.

16. Put tray with samples in appropriate cup locations on autosampler. Position try to the cup containing standard A (usually #35 or so). Select "Start Analysis." Press <enter>.

17. The second screen will ask if the tray has standards or not. If you standardized the first tray of the run and all the check standards are within QC ranges, recalibration for the next tray is <u>not</u> necessary. Select appropriate option. Press <enter>.

18. Press Alt, Esc keys together, to get back to background to view the calibration peaks.

    After calibration is complete:

    - go into the foreground (Press Alt, Esc keys)
    - select "display calibration graph" (Press <enter>)
    - review the data
    - return to the background (Press Alt, Esc keys)

- press "G" for good calibration. Analysis will continue.

- press "R" for re-calibration. Remember to refill standard cups and reposition sample tray before pressing "R"!

B. Instrument Shut-Down

1. Press Alt/Esc keys to get to the foreground. Select "Load/Stop Background Method". Press <enter>. To question-"Stop background (Y/N)?" Press "Yes". Press Esc key to return to main menu.

2. If column is used, stop the pump and disconnect from manifold.

3. Pull lines from reagents into a wash beaker of D.I..

4. Pump D.I. through lines for 2-5 minutes.

5. Pump air through lines until manifold is dry.

6. Turn off pump.

7. Release tubing cartridges and lower tension levers. Release tubing.

8. Turn off main switch on rear power strip.

9. Empty and rinse waste containers, if necessary.

10. Perform back-up on current data files, once a week. (See Section C)

11. Turn off the computer and printer.

C. Backing-up the Data Files

1. Exit to DOS

2. At C> Type: cd\fialab\data Press <enter>

3. At C> Type: copy *.rpt a: Press <enter>
After everything is copied - remove disc.

4. At C> Type: del *.* Press <enter>

5. Are you sure (Y/N)? Type: Y Press <enter>

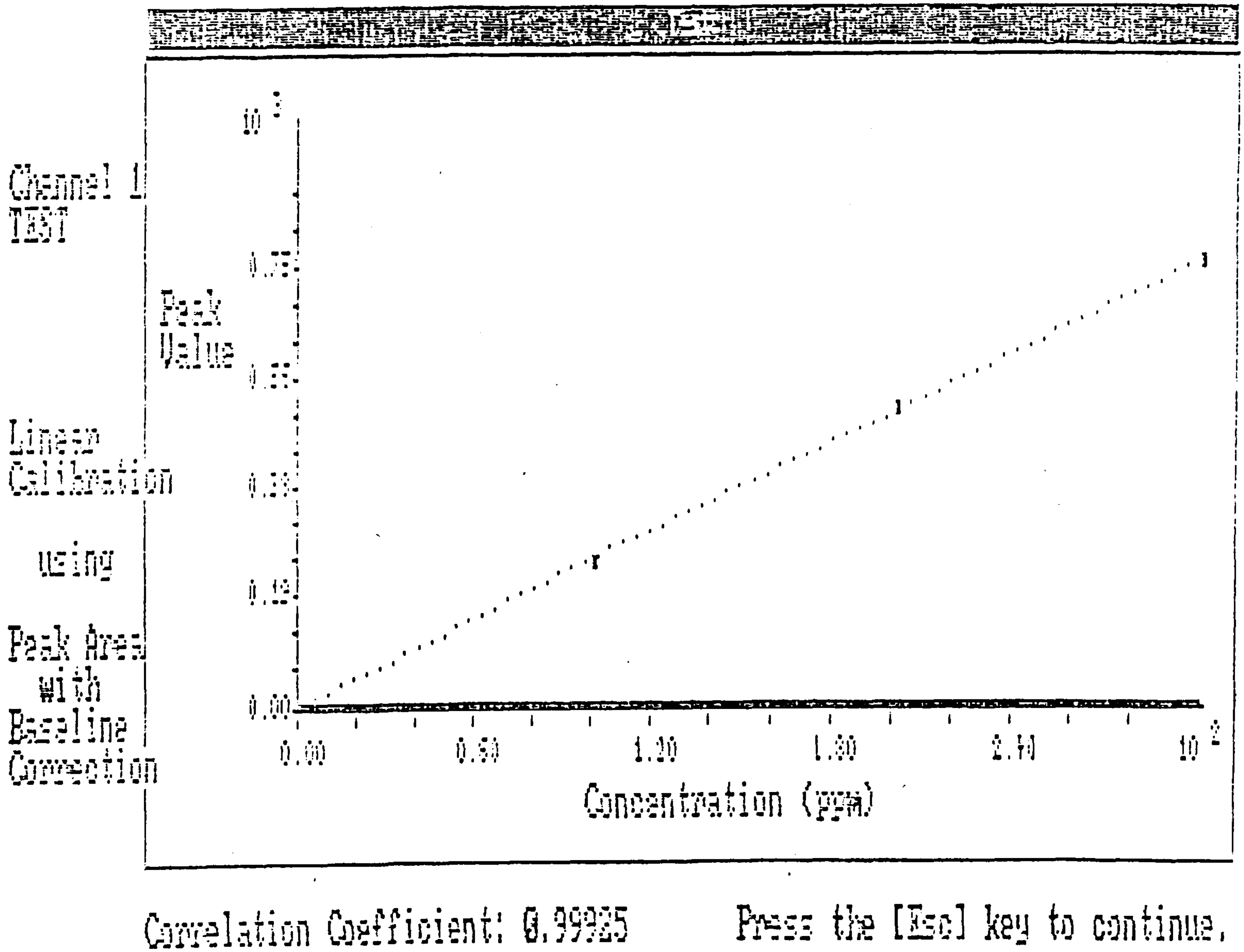
6. At C> Type: cd\ Press <enter>

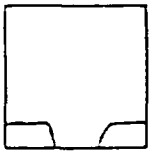
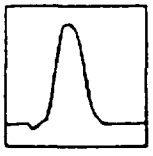
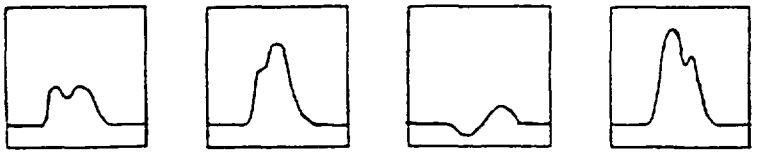
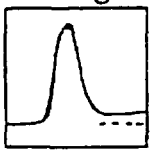
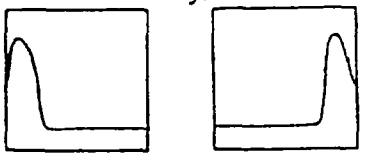
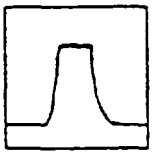
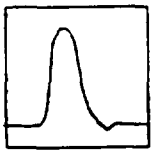
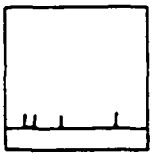
7. Turn off the red switch on the computer power strip to turn off the computer, printer and screen.

D. Quikchem Calibration

QuikCalc II uses a calibration technique called multisegment linear fitting which gives extensive flexibility to the user. It allows the calibration curve to be defined in terms of individual linear segments which can span each of several standards. Following processing of the calibration standards, a correlation coefficient is calculated for each segment with more than two standards or replicates. It provides important statistical information about each segment and gives the user a high degree of confidence in the determined sample values. See Figure 1.

FIGURE 1


Channel 1
TEST
Linear
Calibration
using
Peak Area
with
Baseline
Correction
Peak
Value
0.00
1.20
2.40
Concentration (ppm)
Correlation Coefficient: 0.99925
Press the [Esc] key to continue.

Problem:	Cause:
Negative peak 	1. Contaminated carrier 2. Bad or no SO_4 column or sample extremely high in hardness 3. Samples high in oxidizing agents
Reproduceable dip when valve switches (before peak) 	1. Bad color reagent 2. Could also be valve turning artifact caused by a highly colored reagent
Odd looking peaks 	1. Index of refraction problem, matrix related (usually acid or pH buffering) 2. Also method interferences: high hardness on SO_4 method, oxidizing samples on nitrate method 3. Bad reagents
Shifting baseline 	1. Flow problem 2. Precipitate build-up on SO_4 manifold tubing
Peak too early/late 	1. Usually flow problem 2. Valve not set to an initial load position state before starting run 3. Incorrect pump setting or other timing problem
Peak cut off **in** window 	1. Reagents exceeded-reagents improperly prepared 2. Standards incorrectly prepared
Reproduceable dip after peak 	1. Bad column
Small intermittent peaks 	1. Milli-Q or reagents not degassed properly or adequately 2. Waste line coil not installed (for the methods which require it)

Three basic areas of troubleshooting:

1. Fluidics (clogs, old pump tubing, crimp in manifold tubing)
2. Chemistry
3. Timing (not usually a problem after initial development)

BLH/rff
[rff-genpol-604]

APPENDIX B-2

HARDNESS (WARŹYN)

Effective: 5-23-91

HARDNESS AUTOANALYZER

Scope and Application: This method is applicable to drinking water, surface water, groundwater and wastewater.

References: EPA 1983, Method 130.1
Lachat Instruments 1989, Method 10-301-31-1-B

Detection Limit: 10 mg/L.

Optimum Concentration Range: 10-500 mg/L

Sample Handling: Preserve with HNO_3 to a pH < 2, refrigerate at 4°C and analyze within 6 months of collection.

Instrument Conditions:

1. Pump speed: 35
2. Cycle period: 55 seconds
3. Load period: 30 seconds
4. Inject period: 30 seconds
5. Inject to start of peak period: 18 seconds
6. Inject to end of peak period: 69 seconds
7. Gain: 620
8. Zero: 100
9. Interference filter: 520 nm
10. Sample loop: Microloop
11. Standards for curve set-up: 0, 50, 100, 200, 400, 500 mg/L

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. **Degassed Milli-Q water - 2 options:**

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.

   b. Bubble helium, using the fritted gas dispersion tube, through 20 L Milli-Q water for about 15 minutes. Store in cubitainer.

2. **Stock hardness standard (1000 mg/L):** Place 1.000 g anhydrous calcium carbonate (primary standard) in a liter volumetric flask. Add 1 + 1 HCL, a little at a time, until all the $CaCO_3$ is dissolved. Add 200 mL of D.I. water. Boil for a few minutes to expel CO_2. Cool. Adjust to a pH of 5.4 using 3N NH_4OH or 1 + 1 HCL. Dilute to 1 liter with D.I. water. Refrigerate.

3. **Ammonium Hydroxide (3N):** In a liter flask, dilute 210 mL of concentrated NH_4OH to mark with D.I. water.

4. **Standards:** Prepare in 200 mL volumetric flasks using D.I. water. Preserve with 0.3 mL of HNO_3. Refrigerate.

	Concentration of Standard	Letter Identifier	Volume of Stock Standard	Dilute To
	0 mg/L	A	0 mL	200 mL
	50 mg/L	B	10 mL	200 mL
	100 mg/L	C	20 mL	200 mL
	200 mg/L	D	40 mL	200 mL
	400 mg/L	E	80 mL	200 mL
	500 mg/L	F	100 mL	200 mL
CRDL	10 mg/L		2.0 mL	200 mL

5. **Ammonium chloride buffer (pH = 11.0):** Dissolve 67.6 g of ammonium chloride (NH_4Cl) in 572 mL concentrated ammonium hydroxide (NH_4OH, 29.0%). Transfer to a liter volumetric flask and dilute to the mark with D.I. water. Filter before use to degas solution.

   Note: Prepare and filter in the fume hood.

6. **Calmagite indicator:** Dissolve 0.25 g calmagite in 500 mL of D.I. water. Stir 30 minutes on a magnetic stir plate. Filter through 0.45 micron filter paper, before each use.

7. **Magnesium ethylenediamine-tetraacetate:** Dissolve 0.20 g Mg EDTA magnesium salt in a liter volumetric, dilute to the mark using degassed Milli-Q water. (The sodium salt of Mg EDTA may be substituted.)

Notes:

1. Degas buffer before each run.
2. Filter calmagite through 0.45 micron filter paper before each run.
3. Allow reagents to warm up before starting run.
4. Samples must be diluted to obtain concentrations within the optimum working range.
5. The gain and zero settings are guidelines and must be optimized each day.
6. Any sample with turbidity must be filtered prior to analysis. (Use Whatman #1 or #4 filter paper).
7. Color is an interference, dilute the sample and also spike the dilution to confirm the quality of the result. Record on data sheet.

System Operation:

1. Refer to "Auto Analyzer Operation Start-up Procedure". (IOP# LAAC-Section A).

2. Analyze an initial calibration check standard, a blank, a CRDL standard and a known reference standard at the beginning of each run. The blank must be below the detection limit and standards must be within required control limits before any samples are analyzed.

3. To spike samples mix equal volumes of sample and 400 mg/L standard (E) for a final spike level of 200 mg/L.

4. The calibration check standard is 200 mg/L (D).

5. Refer to "Auto Analyzer Shut-down procedure". (IOP# LAAC-Section B).

Quality Control:

1. Establish a standard curve with the standards listed above. The derived concentration of each standard must be ± 10% of its true value. The derived concentration of the blank must be less than the method detection limit.

2. The CRDL standard concentration should be the method detection limit (MDL). Results must be within acceptable limits of ± the MDL or the instrument must be recalibrated before samples are analyzed.

3. A quality control calibration check standard of 200 mg/L (D) and a blank are to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration check standard and blank are still required. The last samples analyzed in the run are to be the calibration check standard and blank. Standards must be within the acceptable ranges and blanks must be below method detection limit or the samples run after the last acceptable calibration check standard and blank are to be reanalyzed.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicates are to be within acceptable ranges or data must be flagged appropriately.

Calculations:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer.

AUTOANALYZER

Scope and Application: Ions can be readily analyzed by a flow-injection autoanalyzer. The flow injection design gives the system excellent washout characteristics, to prevent carry over and cross contamination. The autoanalyzer is generally more sensitive and accurate than the manual wet-chemistry techniques.

Method: Flow injection

References: Lachat Instruments, 1986.

Sample Handling: See separate SOP's for requirements.

Reagents and Apparatus:

1. Lachat 3-channel autoanalyzer
2. Stock and standard ion solutions
3. Class A volumetric flasks
4. Class A volumetric pipets
5. Milli-Q water
6. Required interference filters
7. Disposable 4 mL cups
8. Automatic sampler
9. Proportioning pump
10. Injection module
11. Colorimeters
12. Manifolds
13. Columns - if needed
14. Helium gas
15. Computer
16. Printer

Procedure:

A. Instrument Set-Up

1. Depress red power switch on power strip located behind the computer terminal. This will turn on the computer, the screen, and the printer.

2. Depress red power switch on rear power strip on Lachat system.

3. Select manifold and make appropriate hydraulic connections.

   Hydraulic connections:

a. Use correct sample loop length to connect. Lines 1, 4.

b. Line 2 is carrier line.

c. Line 3 goes to manifold.

d. Line 5 goes to waste container.

e. Line 6 comes from sample probe.

f. Connect manifold to flow through cell.

Tension levers should be up when pump tubing is inserted. Snap pump tubing cartridges into place.

4. Insert correct filter.

5. Pump Milli-Q water through lines for 5 minutes by depressing the pump ON button. Check for leaks.

6. Computer - At the C> type in "quikcalc". This calls up the Lachat software and puts you at the master menu. Press <enter>.

7. Put lines into reagents and/or degassed Milli-Q water.

8. Computer - Select "Load/Stop Background Method" on the master menu. Press <enter>.

9. Select appropriate method. Press <enter>.

10. Printer should be set at FONT 0.

11. Pump reagents until a steady baseline is achieved.

12. When using a method with a column (SO_4 or NO_3), the column may be inserted at this point. See method SOP's for more details.

13. For each analytical channel, adjust zero knob so that the baseline is near the bottom of the screen (between .000 - .030).

14. Adjust gain while injecting top standard.

    a. Place autosampler probe into the highest standard bottle.

    b. After 20-30 seconds, press cycle button on front panel so that LED light is red. This is the load position.

    c. After 25 seconds (or less depending on sample loop size), press cycle button so that LED light is green. This is the inject position.

d. Adjust gain knob on detector so that peak reading on the colorimetric is 1.700-1.950.

e. Repeat until gain is properly adjusted.

f. Wipe probe and replace the autosampler probe into the sampler.

15. Select menu item by going into foreground. (Press and hold Alt key, then press Esc key).

    a. Select "Sample Tray Information and Start Analysis" on master menu. Press <enter>.

    b. Press <enter> or type in sample tray reference number if it is a tray which has already been typed in.

    c. Enter tray ID and operator. Check "Display Standards Position in Tray" to insure the tray is set-up properly.

    d. Select "Enter Sample ID's". Press <enter>.

    e. Type in sample information. Check standards will automatically be placed in the tray information portion.

    f. Press Esc once to return to menu.

16. Put tray with samples in appropriate cup locations on autosampler. Position try to the cup containing standard A (usually #35 or so). Select "Start Analysis." Press <enter>.

17. The second screen will ask if the tray has standards or not. If you standardized the first tray of the run and all the check standards are within QC ranges, recalibration for the next tray is <u>not</u> necessary. Select appropriate option. Press <enter>.

18. Press Alt, Esc keys together, to get back to background to view the calibration peaks.

    After calibration is complete:

    - go into the foreground (Press Alt, Esc keys)
    - select "display calibration graph" (Press <enter>)
    - review the data
    - return to the background (Press Alt, Esc keys)

- press "G" for good calibration. Analysis will continue.

- press "R" for re-calibration. Remember to refill standard cups and reposition sample tray before pressing "R"!

B. Instrument Shut-Down

1. Press Alt/Esc keys to get to the foreground. Select "Load/Stop Background Method". Press <enter>. To question-"Stop background (Y/N)?" Press "Yes". Press Esc key to return to main menu.

2. If column is used, stop the pump and disconnect from manifold.

3. Pull lines from reagents into a wash beaker of D.I..

4. Pump D.I. through lines for 2-5 minutes.

5. Pump air through lines until manifold is dry.

6. Turn off pump.

7. Release tubing cartridges and lower tension levers. Release tubing.

8. Turn off main switch on rear power strip.

9. Empty and rinse waste containers, if necessary.

10. Perform back-up on current data files, once a week. (See Section C)

11. Turn off the computer and printer.

C. Backing-up the Data Files

1. Exit to DOS

2. At C> Type: cd\fialab\data Press <enter>

3. At C> Type: copy *.rpt a: Press <enter>
After everything is copied - remove disc.

4. At C> Type: del *.* Press <enter>

5. Are you sure (Y/N)? Type: Y Press <enter>

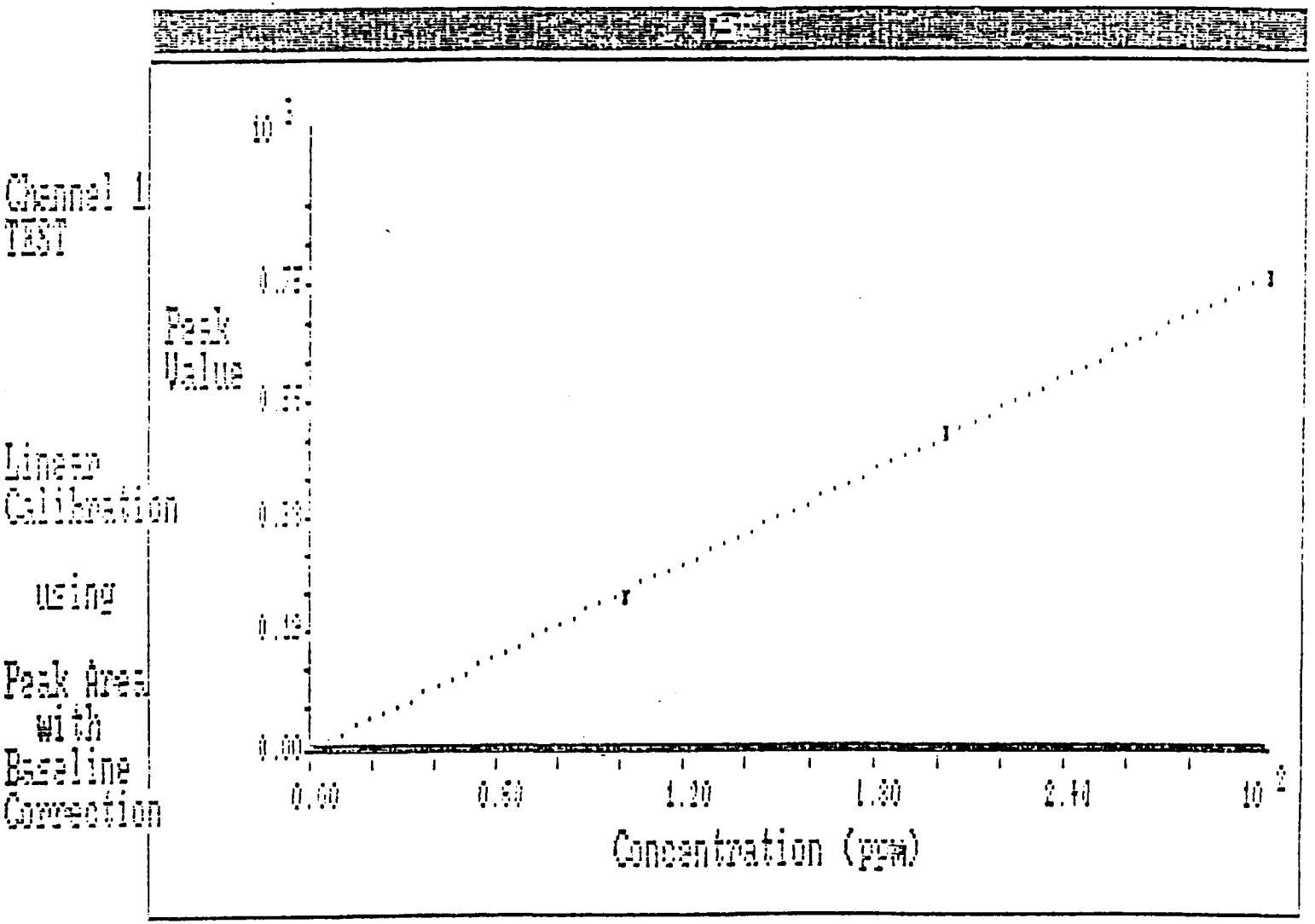
6. At C> Type: cd\ Press <enter>

7. Turn off the red switch on the computer power strip to turn off the computer, printer and screen.

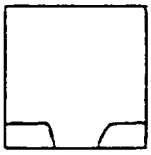
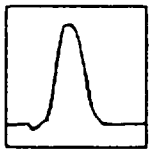
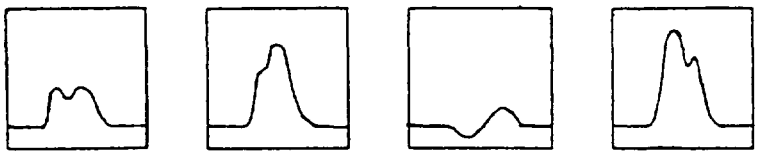
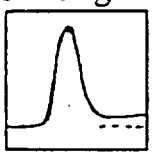
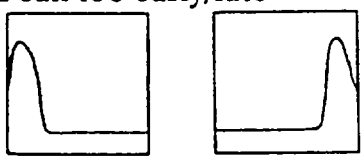
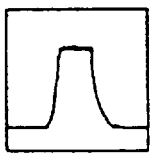
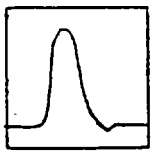
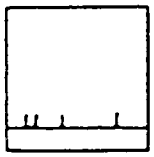
D. Quikchem Calibration

QuikCalc II uses a calibration technique called multisegment linear fitting which gives extensive flexibility to the user. It allows the calibration curve to be defined in terms of individual linear segments which can span each of several standards. Following processing of the calibration standards, a correlation coefficient is calculated for each segment with more than two standards or replicates. It provides important statistical information about each segment and gives the user a high degree of confidence in the determined sample values. See Figure 1.

Multi-Point II Calibration
FIGURE 1



Correlation Coefficient: 0.99935 Press the [Esc] key to continue.

Problem:	Cause:
Negative peak 	1. Contaminated carrier 2. Bad or no SO_4 column or sample extremely high in hardness 3. Samples high in oxidizing agents
Reproduceable dip when valve switches (before peak) 	1. Bad color reagent 2. Could also be valve turning artifact caused by a highly colored reagent
Odd looking peaks 	1. Index of refraction problem, matrix related (usually acid or pH buffering) 2. Also method interferences: high hardness on SO_4 method, oxidizing samples on nitrate method 3. Bad reagents
Shifting baseline 	1. Flow problem 2. Precipitate build-up on SO_4 manifold tubing
Peak too early/late 	1. Usually flow problem 2. Valve not set to an initial load position state before starting run 3. Incorrect pump setting or other timing problem
Peak cut off in window 	1. Reagents exceeded-reagents improperly prepared 2. Standards incorrectly prepared
Reproduceable dip after peak 	1. Bad column
Small intermittent peaks 	1. Milli-Q or reagents not degassed properly or adequately 2. Waste line coil not installed (for the methods which require it)

Three basic areas of troubleshooting:

1. Fluidics (clogs, old pump tubing, crimp in manifold tubing)
2. Chemistry
3. Timing (not usually a problem after initial development)

BLH/rff
[rff-genpol-604]

APPENDIX B-3

AMMONIA NITROGEN (WARZYN)

Effective Date 1-29-90

AMMONIA NITROGEN

Scope and Application: This method is applicable to the determination of ammonia-nitrogen in drinking water, surface water, groundwater, sludges, soils, and industrial wastes.

Method: Micro-distillation, Colorimetric

Reference: EPA, 1983, Method 350.2

Detection Limit: 0.10 mg/L for aqueous samples
5.00 mg/kg for soils and sludges

Optimum Range: 0.10 - 2.00 mg/L for aqueous samples
5.00 - 100 mg/kg for soils and sludges

Sample Handling: Acidify aqueous samples with concentrated sulfuric acid to pH <2 and refrigerate at 4°C. Refrigerate soils and sludges at 4°C. Analyze within 28 days of sampling.

Reagents and Apparatus:

1. Kjeldahl flasks, 100 mL
2. Keeney distillation apparatus
3. Spectrophotometer, set at 425nm with sipper cell
4. Erlenmeyer flasks, 50 mL
5. Sulfuric acid, concentrated
6. Milli-Q water
7. pH meter, 0.1 pH unit sensitivity
8. Volumetric glassware, Class A (pipets and flasks)
9. Top loading balance, 0.01g sensitivity
10. Graduated cylinders, 50 mL
11. Mixing cylinders, 50 mL
12. Ammonium chloride (NH_4Cl)
13. Boric acid (H_3BO_3)
14. Mercuric iodide (HgI_2)
15. Potassium iodide (KI)
16. Sodium hydroxide (NaOH)
17. Sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$)
18. Sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$)
19. Analytical balance, 0.0001g sensitivity
20. 150 mL beaker
21. Stir bars and stir plate

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated).

1. Ammonium chloride stock solution(1000 mg/L): In a 1 liter volumetric flask, dissolve 3.819g NH_4Cl in approximately 300 mL Milli-Q water and bring to volume. Preserve with H_2SO_4 to a pH<2. Refrigerate.

2. Ammonium chloride standard solution (10 mg/L): Dilute 10.0 mL of the ammonium chloride stock solution to 1 liter with Milli-Q water in a volumetric flask. Preserve with H_2SO_4 to a pH<2. Prepare monthly. Refrigerate.

3. Boric acid solution: Dissolve 20.0g H_3BO_3 in Milli-Q water and dilute to 1 liter in a volumetric flask.

4. Nessler reagent: Dissolve 100g of mercuric iodide and 70g of potassium iodide in about 200 mL of Mill-Q water. Add this mixture slowly, while stirring to a COOLED solution of 160g NaOH in 500 mL Milli-Q water. Dilute the mixture to 1 liter. Store in a Pyrex bottle and keep out of direct sunlight. Refrigerate. NOTE: Commercially available.

5. Sodium hydroxide (1N): Dissolve 40g of NaOH in Milli-Q water and dilute to 1 liter.

6. Sodium hydroxide (0.1N): Dilute 100 mL of 1N NaOH to 1 liter with Milli-Q water.

7. Sodium tetraborate solution (0.025M): Dissolve 9.5g of $Na_2B_4O_7 \cdot 10H_2O$ or 5.0g anhydrous $Na_2B_4O_7$ in Milli-Q water and dilute to 1 liter.

8. Borate buffer: Add 88 mL of 0.1N NaOH solution to 500 mL of 0.025M sodium tetraborate solution. Dilute to 1 liter with Milli-Q water.

9. Sodium thiosulfate (1/70N): Dissolve 3.5g $Na_2S_2O_3 \cdot 5H_2O$ in Milli-Q water and dilute to 1 liter. (1 mL of this solution will remove 1 mg/L of residual chlorine in 500 mL of sample).

NOTES:

1. Residual chlorine must be removed prior to distillation by pretreating the sample with sodium thiosulfate solution.

2. Pre-steam the distillation apparatus with 10% NaOH before use.

3. Cyanate and some volatile alkaline compounds may cause an off-color nesslerization. This off-color can be eliminated by boiling the sample at a low pH (pH 2-3) to drive off the compound. This should be done prior to the distillation step.

Procedure: Sample must be homogenized prior to analysis to ensure a representative sample aliquot.

Distillation:

1. All glassware is to be soap and water washed, tap water rinsed, and Milli-Q water rinsed prior to use.

2. The reservoir should be 2/3 full with Milli-Q water. Add a few boiling chips. Add sulfuric acid to reservoir to bring to a pH <2. Turn on the heater. Set heater control to HIGH. Allow the steam reservoir to heat up. This unit will take about 45 minutes to heat-up. Turn the heater control to about a setting of 8 and bring to boiling. Analysis can begin once boiling begins.

3. Prepare the distillation apparatus as follows: Steam out the distillation apparatus with a 10% NaOH solution. Turn on water and continue until 40 mL has been distilled.

4. Aqueous samples:

   Place 50 mL or an aliquot of sample diluted to 50 mL in a 150 mL beaker. Record the volume used. Add 1N NaOH while stirring very slowly until the pH is 9.5 ±0.1 using pH meter.

   To spike: Place 50 mL sample and 5 mL of the 10 mg/L ammonia standard into a beaker, adjust pH to 9.5 ±0.1 and continue with procedure. Final spike level is 1.0 mg/L.

   Non-aqueous samples:

   Place approximately 1.0g in a 150 mL beaker. Record weight used. Add 50 mL Milli-Q water and adjust the pH with 1N NaOH, while stirring slowly, to pH 9.5 ±0.1 using pH meter.

   To spike: Place 1.0g sample, 5 mL of the 10 mg/L ammonia standard in the beaker. Add 50 mL Milli-Q water, adjust pH, and continue with procedure.

5. Transfer the pH-adjusted sample to a 100 mL Kjeldahl flask. Add 2.5 mL of borate buffer.

6. Add 5 mL of boric acid to a 50 mL Erlenmeyer flask and place flask at the condenser outlet with the tip of the condenser immersed in the boric acid.

7. Connect the Kjeldahl flask to the distillation apparatus and secure with springs.

8. Close the stopcock on the condensation chamber. Close the drain stopcock. The steam will now pass through the Kjeldahl flask.

9. Steam distill 30-40 mL at a rate of 4-5 mL/min.

10. Rinse tip of condenser into erlenmeyer flask, remove the erlenmeyer flask.

11. Rinse the tip of the condenser and steam outlet into a waste beaker.

12. Continue distilling remaining samples, blanks and standards. When all samples, blanks and standards are distilled, the colorimetric determination can be performed.

Colorimetric Determination:

1. Prepare the following series of blanks and standards in 50 mL mixing cylinders containing 5 mLs of boric acid solution (These do not need to be taken through the distillation step).

mL of 10 mg/L ammonium chloride solution	Dilute to	Concentration (mg/L)
0	50 mL	BLANK
0.5	50 mL	0.10
1.0	50 mL	0.20
2.0	50 mL	0.40
5.0	50 mL	1.00
10.0	50 mL	2.00

2. Add 2.0 mL of Nessler reagent to the blank and standards. Stopper and mix by inverting several times.

3. After 20 minutes, read the absorbances on the spectrophotometer set at 425nm using the sipper cell. Zero the spectrophotometer to the reagent blank.

4. Transfer distilled samples to 50 mL mixing cylinders and dilute to 50 mL with Milli-Q water. Mix.

5. Determine the ammonia in the distillate as follows:

   - Transfer 25 mL of distillate, or an aliquot diluted to 25 mL, to a mixing cylinder.
   - Add 1 mL of Nessler reagent and mix by inverting several times.
   - After 20 minutes, read the absorbance as described in Step 3.

Calculations:

1. Aqueous Samples:

   a. Calculate using linear regression.

   b. Multiply in any dilution factors performed in the distillation and colorimetric steps to obtain the final result in mg/L.

2. Non-Aqueous Samples:

   a. Calculate using regression to obtain a mg/L value.

   b. Multiply in any dilution factor performed in the colorimetric step (mg/L).

   c. Multiply result obtained from "Step b" by 50 and divide by grams of sample used to obtain the final result in mg/kg.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standards (1.00 mg/L) in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, spectrometer bulb, solutions, etc.).

2. A distilled blank, standard (1.00 mg/L), and known reference standard are to be analyzed at the beginning of the analytical run. The standards must be within acceptable ranges and the blank less then the detection limit, or troubleshooting must be performed.

3. A quality control calibration standard of 1.00 mg/L and a blank are to be analyzed, initially and after every 10 samples. This standard does not need be carried through the distillation procedure. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges ($\pm$ 10% of the true value) or the samples run after the last acceptable check standard are to be reanalyzed.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

APPENDIX B-4

TOTAL DISSOLVED SOLIDS (WARZYN)

Effective Date: 5-3-91

TOTAL DISSOLVED SOLIDS

Scope and Application: This method is applicable to drinking water, surface water, groundwater, and domestic and industrial wastewaters.

Method: Gravimetric, dried at 180°C.

Reference: EPA 1983, Method 160.1

Detection Limit: 10 mg/L (using a 100 mL sample volume)

Sample Handling: Refrigerate at 4°C and analyze sample within 7 days of sampling.

Reagents and Apparatus:

1. Glass fiber filters, Whatman GF/C
2. Gelman filtration funnel and support
3. Suction flask, 1000 mL
4. Porcelain evaporating dishes
5. Volumetric pipet, 50 mL
6. Drying oven at 180°C ± 2°C
7. Desiccator
8. Analytical balance
9. Deionized water

Notes:

1. **Interferences:** Samples with high concentrations of bicarbonate, Ca, Mg, Cl, and SO_4 will require prolonged drying, desiccation, and rapid weighing.

2. Total residue should be < 200 mg. Excessive residue (>200 mg) is difficult to dry thoroughly. Use a smaller volume if TDS is suspected to be high; likewise use a larger volume if TDS is suspected low.

3. Groundwater samples which have already been filtered through a 0.45 micron membrane filter do not need to be carried through the filtration step of the procedure.

Procedure:

1. All glassware is to be soap and water washed, tap rinsed and deionized rinsed prior to analysis.

2. **Evaporating Dish Preparation:** If volatile dissolved solids are also to be analyzed, prepare the evaporating dishes by ashing at 550 ± 50°C for one hour in a muffle furnace.

Otherwise, heat the dishes at 180 ± 2°C for one hour. Cool in desiccator. Weigh. Record the weight. The dishes must be cool before being weighed (about one hour). Repeat this cycle until a constant weight is obtained (± 0.5 mg).

3. **Filter Preparation:** Place the glass fiber filter on the filtration support, place the funnel on top, and wash the filter with three 20 mL portions of deionized water while vacuum is applied. Discard the washings. The filters may be prepared ahead of time. If this is the case, dry them for 1 hour at 103 - 105°C and store in the desiccator until needed.

4. Assemble the filtering apparatus, place a prepared filter on the support and begin suction. Shake the sample and measure out 100 mL in graduated cylinder.

5. Pour sample into filtering apparatus. Apply vacuum until all the sample has been filtered.

6. Pipet 50 mL of filtered sample (less, if the sample is expected to have a high dissolved solids content) into a prepared evaporating dish.

7. Evaporate the sample to dryness in the oven at 180 ± 2°C. Cool in a desiccator for at least one hour and weigh. Repeat the drying cycle until the weight loss is ≤ 0.5 mg.

Quality Control:

1. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicates are to be within acceptable ranges, or data must be flagged appropriately.

2. A blank must be analyzed with every set of samples. (This is a check on contamination, cleanliness of dishes, oven, pipettes, etc.)

3. An EPA or ERA reference standard must be analyzed at the beginning of each analytical run.

Calculations:

$$\text{TDS, mg/L} = \frac{(A-B)}{C} \times 1000000$$

Where A = weight of dish plus residue (g)
B = weight of dish (g)
C = volume of filtered sample used (mL)

APPENDIX B-5

CHLORIDE (WARZYN)

Effective: 5-14-91

CHLORIDE - AUTOANALYZER

Scope and Application: This method is applicable to drinking water, surface water, groundwater and wastewater.

Reference: EPA 1983, Method 325.2
Lachat Instruments 1987, Method 10-117-07-1-B

Detection Limit: 2 mg/L.

Optimum Range: 2 - 100 mg/L

Sample Handling: Refrigerate at 4°C and analyze within 28 days of collection.

Instrument Conditions:

1. Pump speed: 35
2. Cycle period: 30 seconds
3. Load period: 8 seconds
4. Inject period: 15 seconds
5. Inject to start of peak period: 8 seconds
6. Inject to end of peak period: 31 seconds
7. Gain: 200
8. Zero: 250
9. Interference filter: 480 nm
10. Sample loop: 20 cm
11. Standards for curve set-up: 0, 10, 20, 50, 80, and 100 mg/L

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated.)

1. Degassed Milli-Q water - 2 options:

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.

   b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water (15 min/20 L.) Store in cubitainer.

2. **Stock chloride standard (1000 mg/L):** Dry 2 g of primary grade sodium chloride (NaCl) at 140°C overnight. In a 1 liter volumetric flask, dissolve 1.648 g of dried primary grade sodium chloride (NaCl) in 500 mL D.I. water. Dilute to the mark and invert to mix. Refrigerate.

3. **Standards:** (Prepare fresh every month). Dilute to volume using D.I. water. Refrigerate.

Concentration of Standard	Letter Identifier	Volume of Chloride Stock (ml)	Dilute to
0 mg/L	A	0	200 mL
10 mg/L	B	2.0	200 mL
20 mg/L	C	4.0	200 mL
50 mg/L	D	25	500 mL
80 mg/L	E	40	500 mL
100 mg/L	F	20	200 mL
CRDL 2 mg/L		2.0	1000 mL

Note: Computer refers to standards by letter. Final volumes are not the same!

4. **Stock mercuric thiocyanate reagent:** In a 1 liter volumetric flask, dissolve 4.17 g of mercuric thiocyanate ($Hg(SCN)_2$) in one liter of methanol. Invert to mix. Store in amber glass. Refrigerate.

   Caution: Mercury is a very toxic metal. **Wear gloves!**

5. **Stock ferric nitrate reagent (0.5M):** In a 1 liter volumetric flask, dissolve 202.0 g of ferric nitrate $(Fe(NO_3)_3) \cdot 9H_2O$ in approximately 800 mL of deionized water. Add 25 mL of concentrated nitric acid and dilute to one liter. Invert to mix. Refrigerate.

6. **Combined color reagent:** Mix 150 mL of stock mercuric thiocyanate solution with 150 mL of stock ferric nitrate reagent and dilute to 1000 mL with deionized water. Vacuum filter through a 0.45 micron membrane filter. Store at room temperature. Do Not Refrigerate.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum working range.

2. The gain and zero settings are guidelines and must be optimized each day.

3. The chloride standards may be combined with alkalinity and sulfate standards for use with the 3 channel method.

4. Any sample with turbidity must be filtered prior to analysis. (Use Whatman #1 or #4 filter paper.) Record on data sheet.

5. Color is an interference, dilute the sample and also spike the dilution to confirm the quality of the result. Record on the data sheet.

System Operation:

1. Refer to "Auto Analyzer Operation start-up procedure." (IOP# LAAC Section A).

2. Analyze an initial calibration check standard, a blank, a CRDL standard and a known reference standard at the beginning of each run. The blank must be below the detection limit and the standards must be within required control limits before any samples are analyzed.

3. To spike samples, mix equal volumes of sample and 80 mg/L Cl standard (E) for a final spike level of 40 mg/L Cl.

4. The calibration check standard is 50 mg/L (D).

5. Refer to "Auto Analyzer shut-down procedure". (IOP# LAA-Section B).

Quality Control:

1. Establish a standard curve with the standards listed above. Note that the calibration curve is calculated in a "piece-wise" fashion and is not linear. Be sure that calibration points describe a smooth curve.

2. The CRDL standard concentration should be at the method detection limit (MDL). Results must be within the acceptable limits of ± the MDL or the instrument must be re-calibrated before samples are analyzed.

3. A quality control calibration standard of 50.0 mg/L and a blank are to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicates are to be within acceptable ranges or data must be flagged appropriately.

Calculation:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer. See LAA SOP for further detail.

AUTOANALYZER

Scope and Application: Ions can be readily analyzed by a flow-injection autoanalyzer. The flow injection design gives the system excellent washout characteristics, to prevent carry over and cross contamination. The autoanalyzer is generally more sensitive and accurate than the manual wet-chemistry techniques.

Method: Flow injection

References: Lachat Instruments, 1986.

Sample Handling: See separate SOP's for requirements.

Reagents and Apparatus:

1. Lachat 3-channel autoanalyzer
2. Stock and standard ion solutions
3. Class A volumetric flasks
4. Class A volumetric pipets
5. Milli-Q water
6. Required interference filters
7. Disposable 4 mL cups
8. Automatic sampler
9. Proportioning pump
10. Injection module
11. Colorimeters
12. Manifolds
13. Columns - if needed
14. Helium gas
15. Computer
16. Printer

Procedure:

A. Instrument Set-Up

1. Depress red power switch on power strip located behind the computer terminal. This will turn on the computer, the screen, and the printer.

2. Depress red power switch on rear power strip on Lachat system.

3. Select manifold and make appropriate hydraulic connections.

   Hydraulic connections:

a. Use correct sample loop length to connect. Lines 1, 4.

b. Line 2 is carrier line.

c. Line 3 goes to manifold.

d. Line 5 goes to waste container.

e. Line 6 comes from sample probe.

f. Connect manifold to flow through cell.

Tension levers should be up when pump tubing is inserted. Snap pump tubing cartridges into place.

4. Insert correct filter.

5. Pump Milli-Q water through lines for 5 minutes by depressing the pump ON button. Check for leaks.

6. Computer - At the C> type in "quikcalc". This calls up the Lachat software and puts you at the master menu. Press <enter>.

7. Put lines into reagents and/or degassed Milli-Q water.

8. Computer - Select "Load/Stop Background Method" on the master menu. Press <enter>.

9. Select appropriate method. Press <enter>.

10. Printer should be set at FONT 0.

11. Pump reagents until a steady baseline is achieved.

12. When using a method with a column (SO_4 or NO_3), the column may be inserted at this point. See method SOP's for more details.

13. For each analytical channel, adjust zero knob so that the baseline is near the bottom of the screen (between .000 - .030).

14. Adjust gain while injecting top standard.

    a. Place autosampler probe into the highest standard bottle.

    b. After 20-30 seconds, press cycle button on front panel so that LED light is red. This is the load position.

    c. After 25 seconds (or less depending on sample loop size), press cycle button so that LED light is green. This is the inject position.

d. Adjust gain knob on detector so that peak reading on the colorimetric is 1.700-1.950.

e. Repeat until gain is properly adjusted.

f. Wipe probe and replace the autosampler probe into the sampler.

15. Select menu item by going into foreground. (Press and hold Alt key, then press Esc key).

    a. Select "Sample Tray Information and Start Analysis" on master menu. Press <enter>.

    b. Press <enter> or type in sample tray reference number if it is a tray which has already been typed in.

    c. Enter tray ID and operator. Check "Display Standards Position in Tray" to insure the tray is set-up properly.

    d. Select "Enter Sample ID's". Press <enter>.

    e. Type in sample information. Check standards will automatically be placed in the tray information portion.

    f. Press Esc once to return to menu.

16. Put tray with samples in appropriate cup locations on autosampler. Position try to the cup containing standard A (usually #35 or so). Select "Start Analysis." Press <enter>.

17. The second screen will ask if the tray has standards or not. If you standardized the first tray of the run and all the check standards are within QC ranges, recalibration for the next tray is <u>not</u> necessary. Select appropriate option. Press <enter>.

18. Press Alt, Esc keys together, to get back to background to view the calibration peaks.

    After calibration is complete:

    - go into the foreground (Press Alt, Esc keys)
    - select "display calibration graph" (Press <enter>)
    - review the data
    - return to the background (Press Alt, Esc keys)

- press "G" for good calibration. Analysis will continue.

- press "R" for re-calibration. Remember to refill standard cups and reposition sample tray before pressing "R"!

B. Instrument Shut-Down

1. Press Alt/Esc keys to get to the foreground. Select "Load/Stop Background Method". Press <enter>. To question-"Stop background (Y/N)?" Press "Yes". Press Esc key to return to main menu.

2. If column is used, stop the pump and disconnect from manifold.

3. Pull lines from reagents into a wash beaker of D.I..

4. Pump D.I. through lines for 2-5 minutes.

5. Pump air through lines until manifold is dry.

6. Turn off pump.

7. Release tubing cartridges and lower tension levers. Release tubing.

8. Turn off main switch on rear power strip.

9. Empty and rinse waste containers, if necessary.

10. Perform back-up on current data files, once a week. (See Section C)

11. Turn off the computer and printer.

C. Backing-up the Data Files

1. Exit to DOS

2. At C> Type: cd\fialab\data Press <enter>

3. At C> Type: copy *.rpt a: Press <enter>
After everything is copied - remove disc.

4. At C> Type: del *.* Press <enter>

5. Are you sure (Y/N)? Type: Y Press <enter>

6. At C> Type: cd\ Press <enter>

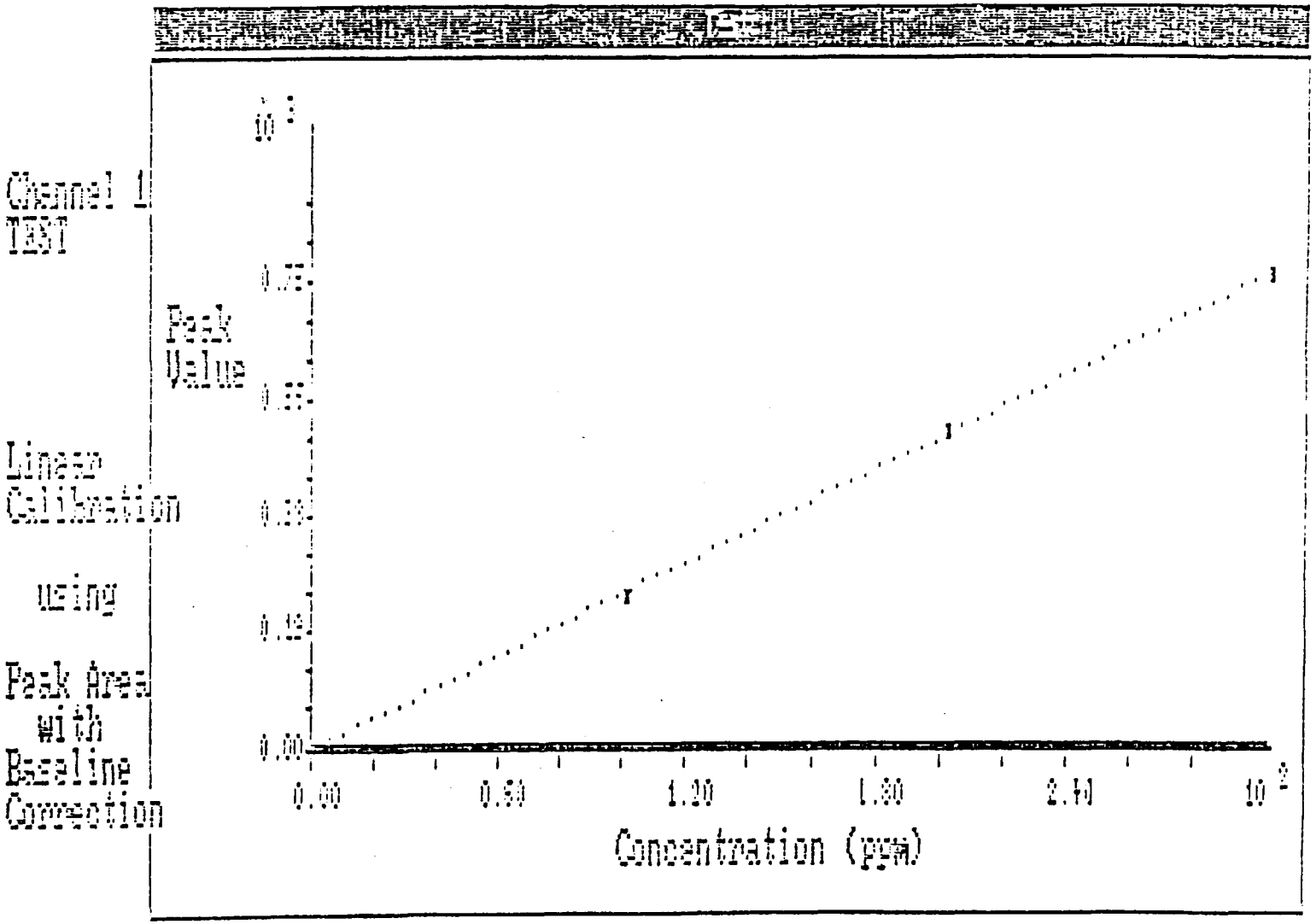
7. Turn off the red switch on the computer power strip to turn off the computer, printer and screen.

D. Quikchem Calibration

QuikCalc II uses a calibration technique called multisegment linear fitting which gives extensive flexibility to the user. It allows the calibration curve to be defined in terms of individual linear segments which can span each of several standards. Following processing of the calibration standards, a correlation coefficient is calculated for each segment with more than two standards or replicates. It provides important statistical information about each segment and gives the user a high degree of confidence in the determined sample values. See Figure 1.

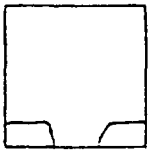
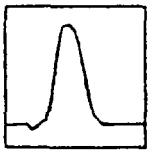
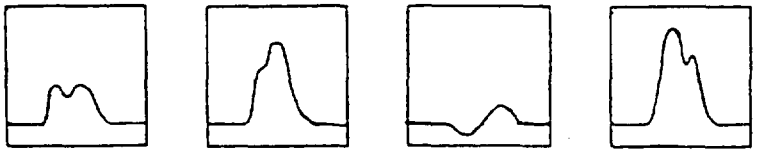
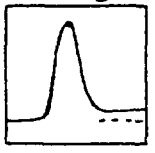
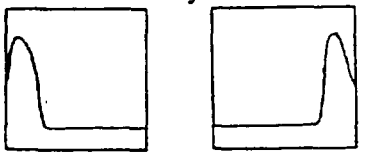
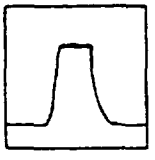
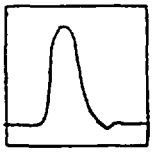
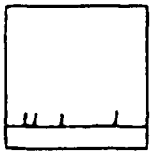
Calibration II Calibration

FIGURE 1



Correlation Coefficient: 0.99925

Press the [Esc] key to continue.

Problem:	Cause:
Negative peak 	1. Contaminated carrier 2. Bad or no SO_4 column or sample extremely high in hardness 3. Samples high in oxidizing agents
Reproduceable dip when valve switches (before peak) 	1. Bad color reagent 2. Could also be valve turning artifact caused by a highly colored reagent
Odd looking peaks 	1. Index of refraction problem, matrix related (usually acid or pH buffering) 2. Also method interferences: high hardness on SO_4 method, oxidizing samples on nitrate method 3. Bad reagents
Shifting baseline 	1. Flow problem 2. Precipitate build-up on SO_4 manifold tubing
Peak too early/late 	1. Usually flow problem 2. Valve not set to an initial load position state before starting run 3. Incorrect pump setting or other timing problem
Peak cut off **in** window 	1. Reagents exceeded-reagents improperly prepared 2. Standards incorrectly prepared
Reproduceable dip after peak 	1. Bad column
Small intermittent peaks 	1. Milli-Q or reagents not degassed properly or adequately 2. Waste line coil not installed (for the methods which require it)

Three basic areas of troubleshooting:

1. Fluidics (clogs, old pump tubing, crimp in manifold tubing)
2. Chemistry
3. Timing (not usually a problem after initial development)

BLH/rff
[rff-genpol-604]

APPENDIX B-6

SULFATE (WARZYN)

Effective: 5-23-91

SULFATE - AUTOANALYZER

Scope and Application: This method is applicable to drinking water, surface water, groundwater and wastewater.

Reference: EPA 1989, Method 375.2
Lachat Instruments 1989, Method 10-116-10-2-B

Detection Limit: 10 mg/L.

Optimum Range: 10 - 200 mg/L

Sample Handling: Refrigerate at 4°C and analyze within 28 days of collection.

Instrument Conditions:

1. Pump speed: 35 seconds
2. Load period: 10 seconds
3. Inject period: 30 seconds
4. Inject to start of peak period: 10 seconds
5. Inject to end of peak period: 56 seconds
6. Cycle period: 50 seconds
7. Gain: 700
8. Zero: 200
9. Interference filter: 460 nm
10. Sample loop: 10 cm
11. Standards for curve set-up: 0, 25, 50, 100, 150, 200 mg/L.

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated.)

1. **Degassing with helium - 2 options:**

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.
   b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water (15 min/20 L.) Store in cubitainer.

2. **Carrier (0.3 ppm SO_4):** In a 1 liter volumetric flask, add 0.3 mL of 1000 ppm stock sulfate solution and dilute to mark with degassed Milli-Q water.

3. **Barium chloride solution (6.24mM):** In a 1 liter volumetric flask, dissolve 1.526 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in 500 mL of Milli-Q water and dilute to 1 liter.

4. **Hydrochloric acid (1.0N):** In a 100 mL volumetric flask, containing approximately 80 mL of Milli-Q water, add 8.3 mL of concentrated hydrochloric acid and dilute to the mark with Milli-Q water.

5. **Barium - MTB color reagent:** (The purity of the methylthymol blue and the alcohol can be critical. **Use the sources stated below**).

In a dry 1000 mL volumetric flask, place 0.2364* g of methylthymol blue (3', 3" bis-N, N-bis carboxymethyl)-amino methylthymolsulfon-ephthalein pentasodium salt (Kodak No. 8068). Add 50 mL of barium chloride solution ("3" above). The solution may be used to aid in the transfer of the dye. Swirl to dissolve. Add 8.0 mL of the 1.0N HCL solution ("4" above) and mix - solution may turn orange. Add 142 mL deionized water and dilute to 1000 mL with ethanol (Aldrich 24.511.9) Mix. The pH of this solution should be 2.5. Prepare this solution the day before use and store it refrigerated in an amber bottle.

* Strength of reagent varies with lot number. The optimum weight of reagent used must be determined specifically for each new lot of MTB to maintenance consistent method sensitivity. This weight is determined by Lachat and supplied with each batch purchased.

6. **Sodium hydroxide (50% stock solution): Cautiously** dissolve 500 g of sodium hydroxide (NaOH) in 600 mL of Milli-Q water. Cool and dilute to 1 liter. Store in plastic bottle. **Caution: The solution will become very hot!**

7. **Sodium hydroxide (0.18 N):** In a 1 liter volumetric flask, add 14.4 mL of 50% sodium hydroxide ("6" above) to degassed Milli-Q water, and dilute to the mark.

8. **Buffered EDTA (for cleaning manifold):** In a 1 liter volumetric flask, dissolve 6.75 g ammonium chloride (NH_4Cl) in 500 mL DI water. Add 57 mL concentrated ammonium hydroxide and 40.0 g tetrasodium EDTA dihydrate. Dissolve by swirling; dilute to the mark with DI water.

9. **Sulfate stock (1000 mg/L):** Dry approximately 2 g of sodium sulfate (Na_2SO_4) at 105°C for 2 hours. Cool in a desiccator. In a 1 liter volumetric flask, dissolve 1.479 g of the dried sodium sulfate in Milli-Q water and dilute to 1 liter. (1.0 mL = 1.0 mg SO_4).

10. **Working standard:** (Prepare fresh every month). Dilute to volume using degassed Milli-Q water. Refrigerate.

Concentration of Standard	Letter Identifier	Volume of Sulfate Standard	Dilute to
0 mg/L	A	0	200 mL
25 mg/L	B	5.0	200 mL
50 mg/L	C	10	200 mL
100 mg/L	D	50	500 mL
150 mg/L	E	75	500 mL
200 mg/L	F	40	200 mL
CRDL 10 mg/L		2.0	200 mL

Note: Final volumes are not the same! Computer refers to standards by letter.

Preparation of Ion Exchange Column:

1. Make a slurry of approximately 0.5 g of BioRex 70, 50-100 mesh ion exchange resin in Milli-Q water.

2. Remove one column end from the glass column. Fill the column with water, then aspirate the slurry or allow it to settle by gravity to pack the column. Take care to **avoid trapping air bubbles** in the column and its fittings at this point and all subsequent operations.

3. After the resin has settled, replace the end fitting. To ensure a good seal, remove any resin particles from the threads of the glass, the column end and the end fittings. To store the column, the ends of the Teflon tubing may be joined with a union.

4. To test the effectiveness of the column, make up a standard of pure sodium sulfate and compare its peak height to an identical standard with hardness typical of the samples added. If the column is being depleted, the standard with hardness will read lower because the divalent cations are complexing the free MTB. The concentration of the standard should be mid-range. If depletion has occurred, repack the column with fresh resin.

5. **Regenerating Resin:** Batch regeneration is recommended because the hydrogen form of BioRex 70 can swell considerable more than the sodium form. Collect the used resin in a small beaker or flask. Wash with dilute HCL until the wash tests free of calcium and/or magnesium. This procedure removes the divalent cations by converting the carboxylate exchange group to the protonated form - COOH. Convert the resin back to the sodium form by neutralizing with washes of 0.5M NaOH until the wash has a pH of 9 or greater. Rinse with deionized water for storage or repacking. A column may be used for 3-4 trays (approximately 150 samples) before it needs to be replaced.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum working range.

2. Sulfate standards may be combined with alkalinity and chloride standards for use with the 3-channel method.

3. The gain and zero settings are guidelines and must be optimized each day.

4. All coils (including waste coil) must be changed at least once each quarter to prevent build-up in lines.

4. **Interferences:**

   - The cation exchange column removes multivalent cations. Run a mid-range sulfate standard containing a typical concentration of $CaCO_3$ periodically to check performance. Any decrease in peak height should indicate the need to regenerate or replace the resin. (At 600 ppm $CaCO_3$, the column is good for 80 + injections.)

- Samples with pH < 2 should be neutralized. High acid concentrations can displace multivalent cations from the column.

- Color will interfere. Dilute the sample and also spike the dilution to confirm the quality of the result. Record on the data sheet.

- Turbidity - turbid samples may be filtered (use Whatman #1 or #4 filter paper) prior to analysis on Lachat.

- Orthophosphate also forms a precipitate with barium at high pH. Check the response of pure orthophosphate standards, if samples are known to be high in phosphate.

5. **Troubleshooting:** Baseline noise with reagents pumping.

   a. Noise with column in line but good baseline without column.

      - Repack column, **air bubbles** may be causing pulsing.

      - Check flow fit connectors and end fittings on column for blockage or leaks.

   b. Noise with and without column in line.

      - Degas carrier and/or reagents. Fine bubbles cause sharp spikes on baseline.

      - Place a longer piece of manifold tubing on the outlet of the flow cell leading to the waste container. This method requires the use of the screw type flow cell.

      - Replace the pump tubes. The **silicone tube,** used for the color reagent, wears faster than the PVC pump tubes.

      - With water pumping in the lines, check all hydraulic connections for blockages, leaks, etc.

Baseline drift:

1. Clean the manifold with the buffered EDTA.

2. Turn the gain high and use the shortest sample loop possible. This improves the linearity of the calibration curve, prolongs the useful life of the column, and minimizes the build up of $BaSO_4$ on the manifold tubing.

System Operation:

1. Refer to "Auto Analyzer Operation start-up procedure." (SOP# LAAC-Section A).

2. Pump reagents through the lines **before** inserting the column. Use a short piece of manifold tubing in place of the column. When all air has passed and the baseline is steady, turn **off** the pump and insert the column. The column should be placed in a vertical position with flow in the top and out the bottom. In this configuration, the column will operate effectively even if the resin packs down more to leave a gap at the top. Resume pumping.

3. Analyze an initial calibration check standard, a blank, a CRDL standard and a known reference at the beginning of each run. The blank must be less than the detection limit and the standards must be within required control limits before any samples are analyzed.

4. **To spike:** Mix equal volumes of sample and 150 mg/L standard (E) for a final spike level of 75 mg/L.

5. The calibration check standard is 100 mg/L (D).

6. To shut down, turn off pump and remove the column.

   To remove the column:

   a. Turn off the pump.
   b. Remove the column.
   c. Join ends of the column with a union.
   d. Replace the column on the manifold with the short teflon tubing piece.
   e. Rinse manifold with Milli-Q water.
   f. Rinse manifold with EDTA cleaning solution.
   g. Continue with "Auto Analyzer Shut-down procedures" (SOP # LAAC-Section B).

Quality Control:

1. Establish a standard curve with the standards listed above. Note that the calibration curve is calculated in a "piece-wise" fashion and is not linear. Be sure that calibration points describe smooth curve. If not, necessary troubleshooting must be performed before continuing (check reagents, pump tubing, valves, etc.).

2. The CRDL standard concentration should be at the method detection limit (MDL). Results must be within the acceptable limits of ± the MDL or the instrument must be recalibrated before samples are analyzed.

3. A quality control calibration check standard of 100 mg/L and a blank are to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration check standard and blank are still required. The last samples analyzed in the run are to be the calibration check standard and blank. Standards must be within the acceptable ranges and blanks must be below the method detection limit or the samples run after the last acceptable calibration check standard and blank are to be reanalyzed.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicates are to be within acceptable ranges or data must be flagged appropriately.

Calculation:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer. See LAAC SOP for further detail.

AUTOANALYZER

Scope and Application: Ions can be readily analyzed by a flow-injection autoanalyzer. The flow injection design gives the system excellent washout characteristics, to prevent carry over and cross contamination. The autoanalyzer is generally more sensitive and accurate than the manual wet-chemistry techniques.

Method: Flow injection

References: Lachat Instruments, 1986.

Sample Handling: See separate SOP's for requirements.

Reagents and Apparatus:

1. Lachat 3-channel autoanalyzer
2. Stock and standard ion solutions
3. Class A volumetric flasks
4. Class A volumetric pipets
5. Milli-Q water
6. Required interference filters
7. Disposable 4 mL cups
8. Automatic sampler
9. Proportioning pump
10. Injection module
11. Colorimeters
12. Manifolds
13. Columns - if needed
14. Helium gas
15. Computer
16. Printer

Procedure:

A. Instrument Set-Up

1. Depress red power switch on power strip located behind the computer terminal. This will turn on the computer, the screen, and the printer.

2. Depress red power switch on rear power strip on Lachat system.

3. Select manifold and make appropriate hydraulic connections.

   Hydraulic connections:

a. Use correct sample loop length to connect. Lines 1, 4.

b. Line 2 is carrier line.

c. Line 3 goes to manifold.

d. Line 5 goes to waste container.

e. Line 6 comes from sample probe.

f. Connect manifold to flow through cell.

Tension levers should be up when pump tubing is inserted. Snap pump tubing cartridges into place.

4. Insert correct filter.

5. Pump Milli-Q water through lines for 5 minutes by depressing the pump ON button. Check for leaks.

6. Computer - At the C> type in "quikcalc". This calls up the Lachat software and puts you at the master menu. Press <enter>.

7. Put lines into reagents and/or degassed Milli-Q water.

8. Computer - Select "Load/Stop Background Method" on the master menu. Press <enter>.

9. Select appropriate method. Press <enter>.

10. Printer should be set at FONT 0.

11. Pump reagents until a steady baseline is achieved.

12. When using a method with a column (SO_4 or NO_3), the column may be inserted at this point. See method SOP's for more details.

13. For each analytical channel, adjust zero knob so that the baseline is near the bottom of the screen (between .000 - .030).

14. Adjust gain while injecting top standard.

    a. Place autosampler probe into the highest standard bottle.

    b. After 20-30 seconds, press cycle button on front panel so that LED light is red. This is the load position.

    c. After 25 seconds (or less depending on sample loop size), press cycle button so that LED light is green. This is the inject position.

d. Adjust gain knob on detector so that peak reading on the colorimetric is 1.700-1.950.

e. Repeat until gain is properly adjusted.

f. Wipe probe and replace the autosampler probe into the sampler.

15. Select menu item by going into foreground. (Press and hold Alt key, then press Esc key).

    a. Select "Sample Tray Information and Start Analysis" on master menu. Press <enter>.

    b. Press <enter> or type in sample tray reference number if it is a tray which has already been typed in.

    c. Enter tray ID and operator. Check "Display Standards Position in Tray" to insure the tray is set-up properly.

    d. Select "Enter Sample ID's". Press <enter>.

    e. Type in sample information. Check standards will automatically be placed in the tray information portion.

    f. Press Esc once to return to menu.

16. Put tray with samples in appropriate cup locations on autosampler. Position try to the cup containing standard A (usually #35 or so). Select "Start Analysis." Press <enter>.

17. The second screen will ask if the tray has standards or not. If you standardized the first tray of the run and all the check standards are within QC ranges, recalibration for the next tray is <u>not</u> necessary. Select appropriate option. Press <enter>.

18. Press Alt, Esc keys together, to get back to background to view the calibration peaks.

    After calibration is complete:

    - go into the foreground (Press Alt, Esc keys)
    - select "display calibration graph" (Press <enter>)
    - review the data
    - return to the background (Press Alt, Esc keys)

- press "G" for good calibration. Analysis will continue.

- press "R" for re-calibration. Remember to refill standard cups and reposition sample tray before pressing "R"!

B. Instrument Shut-Down

1. Press Alt/Esc keys to get to the foreground. Select "Load/Stop Background Method". Press <enter>. To question-"Stop background (Y/N)?" Press "Yes". Press Esc key to return to main menu.

2. If column is used, stop the pump and disconnect from manifold.

3. Pull lines from reagents into a wash beaker of D.I..

4. Pump D.I. through lines for 2-5 minutes.

5. Pump air through lines until manifold is dry.

6. Turn off pump.

7. Release tubing cartridges and lower tension levers. Release tubing.

8. Turn off main switch on rear power strip.

9. Empty and rinse waste containers, if necessary.

10. Perform back-up on current data files, once a week. (See Section C)

11. Turn off the computer and printer.

C. Backing-up the Data Files

1. Exit to DOS

2. At C> Type: cd\fialab\data Press <enter>

3. At C> Type: copy *.rpt a: Press <enter>
After everything is copied - remove disc.

4. At C> Type: del *.* Press <enter>

5. Are you sure (Y/N)? Type: Y Press <enter>

6. At C> Type: cd\ Press <enter>

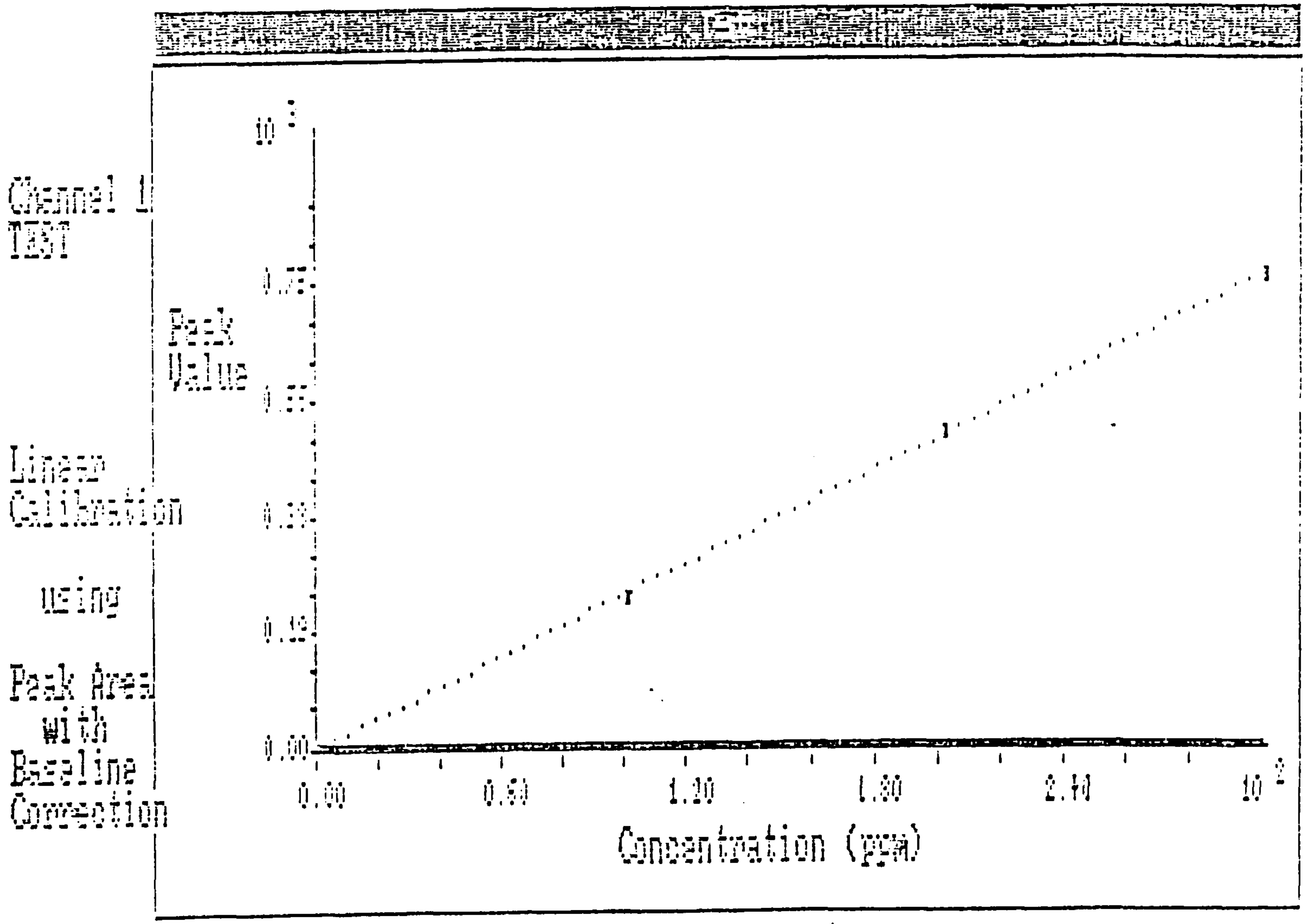
7. Turn off the red switch on the computer power strip to turn off the computer, printer and screen.

D. Quikchem Calibration

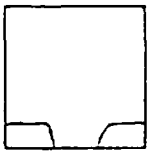
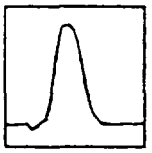
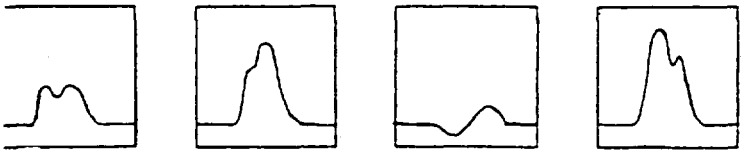
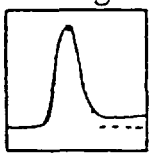
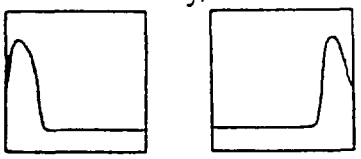
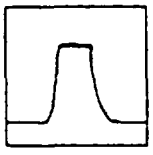
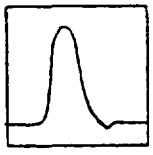
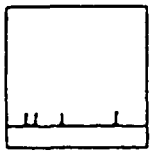
QuikCalc II uses a calibration technique called multisegment linear fitting which gives extensive flexibility to the user. It allows the calibration curve to be defined in terms of individual linear segments which can span each of several standards. Following processing of the calibration standards, a correlation coefficient is calculated for each segment with more than two standards or replicates. It provides important statistical information about each segment and gives the user a high degree of confidence in the determined sample values. See Figure 1.

Qu' 'alc II Calibration

FIGURE 1



Correlation Coefficient: 0.99925   Press the [Esc] key to continue.

Problem:	Cause:
Negative peak 	1. Contaminated carrier 2. Bad or no SO_4 column or sample extremely high in hardness 3. Samples high in oxidizing agents
Reproduceable dip when valve switches (before peak) 	1. Bad color reagent 2. Could also be valve turning artifact caused by a highly colored reagent
Odd looking peaks 	1. Index of refraction problem, matrix related (usually acid or pH buffering) 2. Also method interferences: high hardness on SO_4 method, oxidizing samples on nitrate method 3. Bad reagents
Shifting baseline 	1. Flow problem 2. Precipitate build-up on SO_4 manifold tubing
Peak too early/late 	1. Usually flow problem 2. Valve not set to an initial load position state before starting run 3. Incorrect pump setting or other timing problem
Peak cut off **in** window 	1. Reagents exceeded-reagents improperly prepared 2. Standards incorrectly prepared
Reproduceable dip after peak 	1. Bad column
Small intermittent peaks 	1. Milli-Q or reagents not degassed properly or adequately 2. Waste line coil not installed (for the methods which require it)

Three basic areas of troubleshooting:

1. Fluidics (clogs, old pump tubing, crimp in manifold tubing)
2. Chemistry
3. Timing (not usually a problem after initial development)

BLH/rff
[rff-genpol-604]

APPENDIX B-7

NITRATE NITROGEN (WARZYN)

Effective: 5-22-91

NITRATE + NITRITE, NITROGEN - AUTOANALYZER

Scope and Application: This method is applicable to drinking water, surface water, groundwater, and wastewater.

Reference: EPA 1983, Method 353.2
Lachat Instruments, 1989 Method 10-107-04-1-C

Detection Limit: 0.02 mg/L

Optimum Range: 0.02 - 2.00 mg/L $NO_3 + NO_2$ - N

Sample Handling: Preserve with sulfuric acid to pH < 2 and refrigerate at 4°C. Analyze within 14 days. Alternatively, unpreserved samples, kept at 4°C can be analyzed within 48 hours of sampling.

Instrument Conditions:

1. Pump speed: 35
2. Cycle period: 50 seconds
3. Load period: 20 seconds
4. Inject period: 20 seconds
5. Inject to start of peak period: 22 seconds
6. Inject to end of peak period: 68 seconds
7. Gain: 450
8. Zero: 400
9. Interface filter: 520 nm
10. Sample loop: 17 cm
11. Standards for curve set-up: 0, 0.20, 0.50, 1.00, 2.00 mg/L
12. Column: cadmium reduction

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated.)

1. **Degassed Milli-Q water (2 options):**

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in a cubitainer, or

   b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water. Store in cubitainer. (15 min/20 L)

2. **Stock nitrate standard (100 mg/L NO_3):** In a 1 liter volumetric flask, dissolve 0.7218 potassium nitrate (KNO_3) in about 600 mL of Milli-Q water. Add 2 mL of concentrated H_2SO_4 as a preservative. Dilute to the mark. Store in a dark glass bottle. Refrigerate.

3. **Working stock nitrate standard (10 mg/L NO_3):** Add 50 mLs D.I. water to a 100 mL volumetric flask. Add 0.2 mLs concentrated H_2SO_4 and pipet 10.0 mL of the stock nitrate standard. Dilute to the mark with DI water. Prepare fresh every 2 weeks. Refrigerate.

4. **Standards:** (Prepare fresh every 2 weeks.) Preserve with 0.2 mL H_2SO_4. Dilute to volume with D.I. water. Refrigerate.

	Concentration of Standard	Letter Identifier	Volume of NO_3 Standard	Dilute to
	0 mg/L	A	0	100 mL
	0.20 mg/L	B	2.0	100 mL
	0.50 mg/L	C	5.0	100 mL
	1.00 mg/L	D	10	100 mL
	2.00 mg/L	E	20	100 mL
CRDL	0.02 mg/L		2.0	1000 mL

Note: Computer refers to standards by letter.

5. **Sodium hydroxide (15M):** To 250 mL of D.I. water, add 150.0g NaOH. **Slowly!** This solution will get very HOT! Swirl to dissolve. Store in a plastic bottle.

6. **Ammonium chloride buffer solution:** In a 1 liter volumetric flask, dissolve 85.0g of ammonium chloride (NH_4Cl)* and 1.0g of disodium ethylenediamine tetracetate dihydrate (EDTA) in approximately 800 mL D.I. water. Adjust the pH to 8.5 with 15M NaOH (approximately 8 mL). Dilute to the mark and filter through a 0.45 um filter.

   *** See Notes #5.**

7. **Sulfanilamide color reagent:** In a 1 liter volumetric flask, add approximately 800 mL of Milli-Q water. Then add 100 mL concentrated phosphoric acid (H_3PO_4). Add 40.0g sulfanilamide and dissolve completely. Dissolve 1.0g N-1-naphthlethylenediamine dihydrochloride (NED) and dilute to one liter. Store in **dark bottle** at 4°C. Stable for **2 months** when refrigerated.

8. **Column Preparation:**

   a. **Cadmium preparation:** Place 10-20g of coarse cadmium powder (granules) in a 250 mL beaker and wash with 50 mL of acetone, then distilled water, then two 50 mL portions of 1 M hydrochloric acid (8 mL concentrated hydrochloric acid plus 92 mL deionized water). Then rinse thoroughly with deionized water. If using cadmium for second time, rinse with 1 M hydrochloric acid before beginning process. **CAUTION: Collect and store all waste cadmium. Wear gloves!**

   b. **Copperization:** Prepare a 2% copper sulfate solution (20g of $CuSO_4 \cdot 5H_20$) per liter of deionized water) and add a 100 mL portion to the cadmium prepared in "a" above. Swirl gently for about 5 minutes, then decant the liquid and repeat with a fresh 100 mL portion of 2% copper sulfate. Continue this process until colloidal copper is visible in the supernatant (a red-brown precipitate) and solution remains blue in color. Rinse with D.I. water until all colloidal copper is removed from the supernatant. Wash once with ammonium chloride buffer. The cadmium should be black or dark gray. The cadmium granules may be stored in a stoppered bottle in ammonium chloride buffer.

c. **Packing the column (wear gloves!):** Place a small piece of polyurethane foam (or glass wool) loosely in the end of the glass tube. Insert the plugged end of the glass tube into the column end fitting. Cut a length of 0.032" id teflon tubing 3 to 4 inches longer than the column.

Insert the teflon tube in the end fitting and fill the whole tube with water, holding the flexible tube in a U-shape so that the ends are level. Place the second end fitting on the other end of the teflon tubing. (Placing a small funnel onto the end fitting may aid filling.) Taking care that no air bubbles are introduced, place the copperized cadmium granules in the column. Tap the column gently, every 1-2 cm, to pack the granules. When the column is packed to within about 5 mm of the end of the glass column, insert another foam plug, then the column end fitting. Store the column with the ends connected with a length of teflon tubing, as air pockets or having the column dry out will necessitate repacking. If air remains in the column, connect the column to the manifold and turn the pump on maximum. Tap column firmly until all air is removed.

d. **Column activation:** The column must be activated before use or it will not reduce nitrate. This may be accomplished by pumping the 10 mg/L nitrate standard through the sample line. When the solution is injected, a brilliant pink color will be visible in the coil. The cadmium column efficiency should be above 80%, if less, the column must be repacked.

To check column efficiency, standardize with nitrite standards and then analyze all nitrate standards. The recovery of the nitrate standards should be consistent at all standard concentrations.

Notes:

1. **Interferences:**

   - Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample must be pre-filtered.

   - Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate these interferences.

   - Samples that contain large concentrations of oil and grease will coat the surface of the column. This interference is eliminated by pre-extracting the sample with an organic solvent.

2. Samples must be diluted to obtain concentrations within the optimum working range.

3. The gain and zero settings are guidelines and must be optimized each day.

4. Color will interfere: dilute the sample and also spike the dilution to confirm the quality of the result. Record on data sheet.

5. ACS grade ammonium chloride has been found occasionally to contain significant nitrate contamination, so an alternative preparation for the ammonium chloride buffer (Reagent #6) is as follows:

   In the hood, add 126 mL concentrated HCl to a 1 liter volumetric flask containing 500 mL degassed Milli-Q water. Mix. Add 95 mL ammonium hydroxide and 1.0 gm disodium EDTA. Dissolve and dilute to the mark. The pH should be 8.5 ± 0.1, adjust pH if necessary.

System Operation:

1. Refer to Auto Analyzer Operation - Start-up Procedure (IOP# LAAC-Section A).

2. After pumping reagents through the lines, turn off the pump and insert column, making sure that air bubbles are not introduced into the column.

3. Activate column if necessary. (See #8d. above.)

4. Analyze an initial calibration check standard, a blank, a CRDL standard and a known reference standard at the beginning of each run. The blank must be below the detection limit and standards must be within required control limits before any samples are analyzed.

5. To spike samples, mix equal volumes of sample and 1.00 mg/L standard (D) for a final spike level of 0.50 mg/L.

6. The calibration check standard is 1.00 mg/L NO_3 (D).

7. If only nitrate is requested, nitrites must be analyzed and subtracted from the nitrate + nitrite value.

8. After use, turn off the pump and remove the column from the manifold.

9. Refer to Auto-Analyzer Shut-down Procedure. (IOP# LAAC-Section B.)

Quality Control:

1. Establish a standard curve with the standards listed above. The derived concentrations for each calibration standard must be within 10% of the true value. The derived value for the blank must be below the method detection limit.

2. The CRDL standard concentration should be at the method detection limit (MDL). Results must be within the acceptable limits of ± the MDL of the instrument must be recalibrated before samples are analyzed.

3. A quality control calibration check standard of 1.00 mg/L (D) and a blank are to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration check standard and blank are still required. The last samples analyzed in the run are to be the calibration check standard and blank. Standards must be within the acceptable ranges and blanks must be below the method detection limit or the samples run after the last acceptable calibration check standard and blank are to be reanalyzed.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicates are to be within acceptable ranges or data must be flagged appropriately.

Calculation:

1. Calculate with Lachat Quikchem software, in the concentration mode, using the IBM XT computer.

AUTOANALYZER

Scope and Application: Ions can be readily analyzed by a flow-injection autoanalyzer. The flow injection design gives the system excellent washout characteristics, to prevent carry over and cross contamination. The autoanalyzer is generally more sensitive and accurate than the manual wet-chemistry techniques.

Method: Flow injection

References: Lachat Instruments, 1986.

Sample Handling: See separate SOP's for requirements.

Reagents and Apparatus:

1. Lachat 3-channel autoanalyzer
2. Stock and standard ion solutions
3. Class A volumetric flasks
4. Class A volumetric pipets
5. Milli-Q water
6. Required interference filters
7. Disposable 4 mL cups
8. Automatic sampler
9. Proportioning pump
10. Injection module
11. Colorimeters
12. Manifolds
13. Columns - if needed
14. Helium gas
15. Computer
16. Printer

Procedure:

A. Instrument Set-Up

1. Depress red power switch on power strip located behind the computer terminal. This will turn on the computer, the screen, and the printer.

2. Depress red power switch on rear power strip on Lachat system.

3. Select manifold and make appropriate hydraulic connections.

   Hydraulic connections:

a. Use correct sample loop length to connect. Lines 1, 4.

b. Line 2 is carrier line.

c. Line 3 goes to manifold.

d. Line 5 goes to waste container.

e. Line 6 comes from sample probe.

f. Connect manifold to flow through cell.

Tension levers should be up when pump tubing is inserted. Snap pump tubing cartridges into place.

4. Insert correct filter.

5. Pump Milli-Q water through lines for 5 minutes by depressing the pump ON button. Check for leaks.

6. Computer - At the C> type in "quikcalc". This calls up the Lachat software and puts you at the master menu. Press <enter>.

7. Put lines into reagents and/or degassed Milli-Q water.

8. Computer - Select "Load/Stop Background Method" on the master menu. Press <enter>.

9. Select appropriate method. Press <enter>.

10. Printer should be set at FONT 0.

11. Pump reagents until a steady baseline is achieved.

12. When using a method with a column (SO_4 or NO_3), the column may be inserted at this point. See method SOP's for more details.

13. For each analytical channel, adjust zero knob so that the baseline is near the bottom of the screen (between .000 - .030).

14. Adjust gain while injecting top standard.

    a. Place autosampler probe into the highest standard bottle.

    b. After 20-30 seconds, press cycle button on front panel so that LED light is red. This is the load position.

    c. After 25 seconds (or less depending on sample loop size), press cycle button so that LED light is green. This is the inject position.

d. Adjust gain knob on detector so that peak reading on the colorimetric is 1.700-1.950.

e. Repeat until gain is properly adjusted.

f. Wipe probe and replace the autosampler probe into the sampler.

15. Select menu item by going into foreground. (Press and hold Alt key, then press Esc key).

a. Select "Sample Tray Information and Start Analysis" on master menu. Press <enter>.

b. Press <enter> or type in sample tray reference number if it is a tray which has already been typed in.

c. Enter tray ID and operator. Check "Display Standards Position in Tray" to insure the tray is set-up properly.

d. Select "Enter Sample ID's". Press <enter>.

e. Type in sample information. Check standards will automatically be placed in the tray information portion.

f. Press Esc once to return to menu.

16. Put tray with samples in appropriate cup locations on autosampler. Position try to the cup containing standard A (usually #35 or so). Select "Start Analysis." Press <enter>.

17. The second screen will ask if the tray has standards or not. If you standardized the first tray of the run and all the check standards are within QC ranges, recalibration for the next tray is <u>not</u> necessary. Select appropriate option. Press <enter>.

18. Press Alt, Esc keys together, to get back to background to view the calibration peaks.

After calibration is complete:

- go into the foreground (Press Alt, Esc keys)
- select "display calibration graph" (Press <enter>)
- review the data
- return to the background (Press Alt, Esc keys)

- press "G" for good calibration. Analysis will continue.

- press "R" for re-calibration. Remember to refill standard cups and reposition sample tray before pressing "R"!

B. Instrument Shut-Down

1. Press Alt/Esc keys to get to the foreground. Select "Load/Stop Background Method". Press <enter>. To question-"Stop background (Y/N)?" Press "Yes". Press Esc key to return to main menu.

2. If column is used, stop the pump and disconnect from manifold.

3. Pull lines from reagents into a wash beaker of D.I..

4. Pump D.I. through lines for 2-5 minutes.

5. Pump air through lines until manifold is dry.

6. Turn off pump.

7. Release tubing cartridges and lower tension levers. Release tubing.

8. Turn off main switch on rear power strip.

9. Empty and rinse waste containers, if necessary.

10. Perform back-up on current data files, once a week. (See Section C)

11. Turn off the computer and printer.

C. Backing-up the Data Files

1. Exit to DOS

2. At C> Type: cd\fialab\data Press <enter>

3. At C> Type: copy *.rpt a: Press <enter>
After everything is copied - remove disc.

4. At C> Type: del *.* Press <enter>

5. Are you sure (Y/N)? Type: Y Press <enter>

6. At C> Type: cd\ Press <enter>

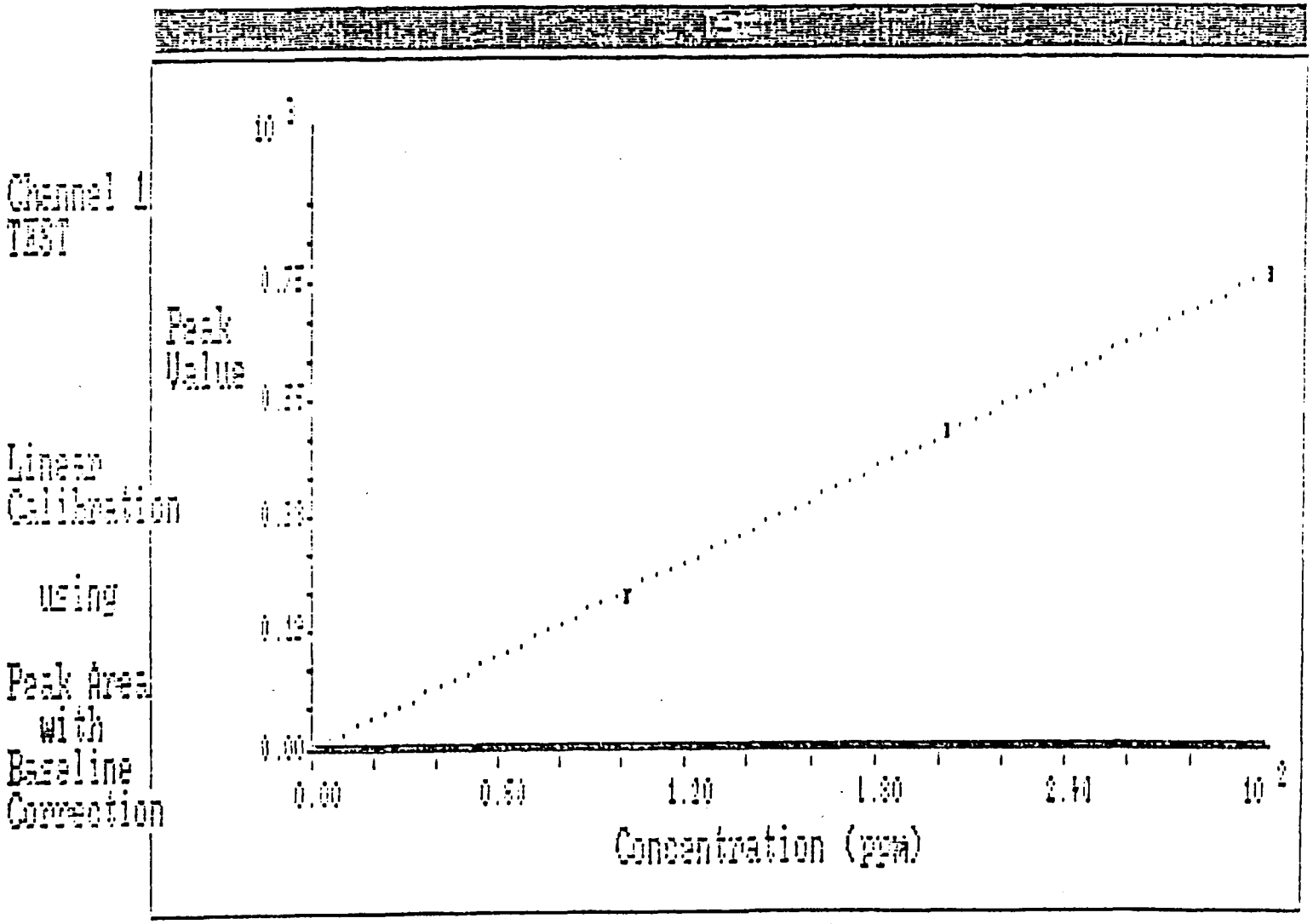
7. Turn off the red switch on the computer power strip to turn off the computer, printer and screen.

D. Quikchem Calibration

QuikCalc II uses a calibration technique called multisegment linear fitting which gives extensive flexibility to the user. It allows the calibration curve to be defined in terms of individual linear segments which can span each of several standards. Following processing of the calibration standards, a correlation coefficient is calculated for each segment with more than two standards or replicates. It provides important statistical information about each segment and gives the user a high degree of confidence in the determined sample values. See Figure 1.

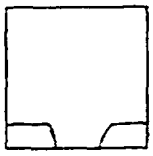
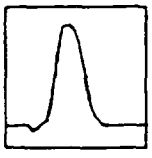
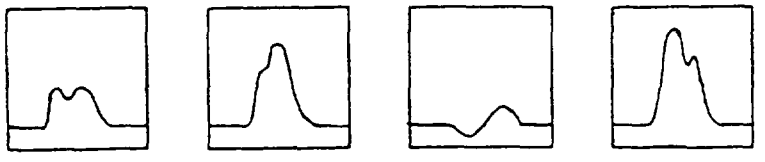
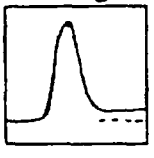
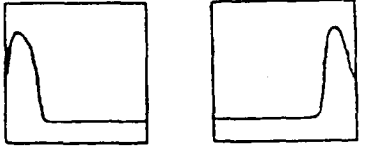
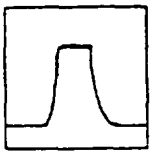
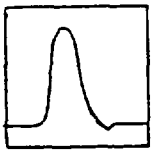
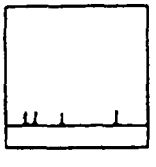
Channel II Calibration

FIGURE 1



Correlation Coefficient: 0.99925

Press the [Esc] key to continue.

Problem:	Cause:
Negative peak 	1. Contaminated carrier 2. Bad or no SO_4 column or sample extremely high in hardness 3. Samples high in oxidizing agents
Reproduceable dip when valve switches (before peak) 	1. Bad color reagent 2. Could also be valve turning artifact caused by a highly colored reagent
Odd looking peaks 	1. Index of refraction problem, matrix related (usually acid or pH buffering) 2. Also method interferences: high hardness on SO_4 method, oxidizing samples on nitrate method 3. Bad reagents
Shifting baseline 	1. Flow problem 2. Precipitate build-up on SO_4 manifold tubing
Peak too early/late 	1. Usually flow problem 2. Valve not set to an initial load position state before starting run 3. Incorrect pump setting or other timing problem
Peak cut off **in** window 	1. Reagents exceeded-reagents improperly prepared 2. Standards incorrectly prepared
Reproduceable dip after peak 	1. Bad column
Small intermittent peaks 	1. Milli-Q or reagents not degassed properly or adequately 2. Waste line coil not installed (for the methods which require it)

Three basic areas of troubleshooting:

1. Fluidics (clogs, old pump tubing, crimp in manifold tubing)
2. Chemistry
3. Timing (not usually a problem after initial development)

BLH/rff
[rff-genpol-604]

APPENDIX B-8

NITRITE NITROGEN (WARZYN)

Effective: 5-22-91

NITRITE, NITROGEN - AUTOANALYZER

Scope and Application: This method is applicable to drinking water, surface water, groundwater and wastewater.

Reference: EPA 1983, Method 353.2
Lachat Instruments, 1989 Method 10-107-04-1-C

Detection Limit: 0.02 mg/L

Optimum Range: 0.02 - 2.00 mg/L NO_2-N.

Sample Handling: Analyze within 48 hours of collection.

Instrument Conditions:

1. Pump speed: 35
2. Cycle period: 40 seconds
3. Load period: 20 seconds
4. Inject period: 20 seconds
5. Inject to start of peak period: 15 seconds
6. Inject to end of peak period: 51 seconds
7. Gain: 300
8. Zero: 400
9. Interference filter: 520 nm
10. Sample loop: 17 cm
11. Standards for curve set-up: 0, 0.20, 0.50, 1.00, 2.00 mg/L

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise stated).

1. **Degassed Milli-Q water (2 options):**

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in a cubitainer.

   b. Bubble helium, using the fritted gas dispersion tube, through the Milli-Q water. Store in a cubitainer. (15 min/20 L).

2. **Stock nitrite standard (100 mg/L NO_2-N):** In a liter volumetric flask, dissolve 0.4926 sodium nitrite ($NaNO_2$) or 0.607g of potassium nitrite (KNO_2) in about 600 mL of Milli-Q water. Add 2 mL of chloroform, as a preservative. Dilute to the mark. Store in refrigerator.

3. **Working stock nitrite standard (10 mg/L NO_2-N):** In a 100 mL volumetric flask, pipet 10.0 mL of the stock nitrite standard and dilute to the mark with Milli-Q water. Standard is good for 2 days when refrigerated, otherwise prepare fresh daily.

4. **Standards:** (Prepare fresh daily). Dilute to volume with Milli-Q water.

	Concentration of Standard	Letter Identifier	Volume of 10 mg/L NO_2 Standard (ml)	Dilute to
	0.00 mg/L	A	0	100 mL
	0.20 mg/L	B	2.0	100 mL
	0.50 mg/L	C	5.0	100 mL
	1.00 mg/L	D	10	100 mL
	2.00 mg/L	E	20	100 mL
CRDL	0.02 mg/L		2.0	1000 mL

Note: Computer refers to standards by letter.

5. **Sodium hydroxide (15M):** To 250 mL of D.I. water, add 150.0g NaOH. **Slowly! This solution will get very HOT!** Swirl to dissolve. Store in a plastic bottle.

6. **Ammonium chloride buffer solution:** In a 1 liter volumetric flask, dissolve 85.0g of Baker Analyzed ammonium chloride* (NH_4Cl) and 1.0g of Aldrich disodium ethylenediamine tetraacetate dihydrate (EDTA) in approximately 800 mL degassed Milli-Q water. Adjust the pH to 8.5 with the 15M NaOH (approximately 8 mL). Dilute to the mark and filter through a 0.45 um filter.

7. **Sulfanilamide color reagent:** In a 1 liter volumetric flask, add approximately 800 mL of degassed Milli-Q water. Then add 100 mL concentrated phosphoric acid (H_3PO_4). Add 40.0g sulfanilamide and dissolve completely. Dissolve 1.0g N-1-Naphthlethylenediamine dihydrochloride (NED) and dilute to one liter. Store in **dark bottle** at 4°C. Stable for **2 months** when refrigerated.

* **See Note #5.**

Notes:

1. Samples must be diluted to obtain concentrations within the optimum working range.

2. The gain and zero settings are guidelines and must be optimized each day.

3. Turbidity will interfere. Samples must be filtered prior to analysis. (Use Whatman #1 or #4 filter paper). Record on data sheet.

4. Color will interfere, dilute the sample and also spike the dilution to confirm the quality of the result. Record on data sheet.

5. ACS grade ammonium chloride has been found occasionally to contain significant nitrate contamination, so an alternative preparation for the ammonium chloride buffer (reagent 6) is as follows:

   In the hood, add 126 mL concentrated HCl to a 1 liter volumetric containing 500 mL degassed Milli-Q water. Mix. Add 95 mL ammonium hydroxide and 1.0 gm disodium EDTA. Dissolve and dilute to the mark. The pH should be 8.5 ± 0.1, adjust pH if necessary.

System Operation:

1. Refer to Auto Analyzer Operation - Start-up Procedure (IOP# LAAC-Section A).

2. Analyze an initial calibration check standard, a CRDL standard, a 0.20 mg/L standard and a blank at the beginning of each run. There are no outside reference standards available for this analyte. The blank must be below the detection limit and the standards must be within required control limits before any samples are analyzed.

3. To spike samples, mix equal volumes of sample and 1.00 mg/L standard (D) for a final spike level of 0.50 mg/L.

4. The calibration check standard is 1.00 mg/L (D).

5. Refer to "Auto Analyzer Shut-Down Procedure". (IOP# LAAC-Section B).

Quality Control:

1. Establish a standard curve with the standards listed above. The derived concentration for each calibration standard must be within 10% of the true value. The derived concentration for the blank must be less than the method detection limit.

2. The CRDL standard concentration should be at the method detection limit (MDL). Results must be within the acceptable limits of ± the MDL of the instrument must be recalibrated before samples are analyzed.

3. A quality control calibration check standard of 1.00 mg/L (D) and a blank are to be analyzed, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration check standard and blank are still required. The last samples analyzed in the run are to be the calibration check standard and blank. These standards must be within the acceptable ranges and blanks must be below the method detection limit or the samples run after the last acceptable calibration check standard and blank are to be reanalyzed.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicates are to be within acceptable ranges or data must be flagged appropriately.

Calculations:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer.

AUTOANALYZER

Scope and Application: Ions can be readily analyzed by a flow-injection autoanalyzer. The flow injection design gives the system excellent washout characteristics, to prevent carry over and cross contamination. The autoanalyzer is generally more sensitive and accurate than the manual wet-chemistry techniques.

Method: Flow injection

References: Lachat Instruments, 1986.

Sample Handling: See separate SOP's for requirements.

Reagents and Apparatus:

1. Lachat 3-channel autoanalyzer
2. Stock and standard ion solutions
3. Class A volumetric flasks
4. Class A volumetric pipets
5. Milli-Q water
6. Required interference filters
7. Disposable 4 mL cups
8. Automatic sampler
9. Proportioning pump
10. Injection module
11. Colorimeters
12. Manifolds
13. Columns - if needed
14. Helium gas
15. Computer
16. Printer

Procedure:

A. Instrument Set-Up

1. Depress red power switch on power strip located behind the computer terminal. This will turn on the computer, the screen, and the printer.

2. Depress red power switch on rear power strip on Lachat system.

3. Select manifold and make appropriate hydraulic connections.

   Hydraulic connections:

a. Use correct sample loop length to connect. Lines 1, 4.

b. Line 2 is carrier line.

c. Line 3 goes to manifold.

d. Line 5 goes to waste container.

e. Line 6 comes from sample probe.

f. Connect manifold to flow through cell.

Tension levers should be up when pump tubing is inserted. Snap pump tubing cartridges into place.

4. Insert correct filter.

5. Pump Milli-Q water through lines for 5 minutes by depressing the pump ON button. Check for leaks.

6. Computer - At the C> type in "quikcalc". This calls up the Lachat software and puts you at the master menu. Press <enter>.

7. Put lines into reagents and/or degassed Milli-Q water.

8. Computer - Select "Load/Stop Background Method" on the master menu. Press <enter>.

9. Select appropriate method. Press <enter>.

10. Printer should be set at FONT 0.

11. Pump reagents until a steady baseline is achieved.

12. When using a method with a column (SO_4 or NO_3), the column may be inserted at this point. See method SOP's for more details.

13. For each analytical channel, adjust zero knob so that the baseline is near the bottom of the screen (between .000 - .030).

14. Adjust gain while injecting top standard.

    a. Place autosampler probe into the highest standard bottle.

    b. After 20-30 seconds, press cycle button on front panel so that LED light is red. This is the load position.

    c. After 25 seconds (or less depending on sample loop size), press cycle button so that LED light is green. This is the inject position.

d. Adjust gain knob on detector so that peak reading on the colorimetric is 1.700-1.950.

e. Repeat until gain is properly adjusted.

f. Wipe probe and replace the autosampler probe into the sampler.

15. Select menu item by going into foreground. (Press and hold Alt key, then press Esc key).

    a. Select "Sample Tray Information and Start Analysis" on master menu. Press <enter>.

    b. Press <enter> or type in sample tray reference number if it is a tray which has already been typed in.

    c. Enter tray ID and operator. Check "Display Standards Position in Tray" to insure the tray is set-up properly.

    d. Select "Enter Sample ID's". Press <enter>.

    e. Type in sample information. Check standards will automatically be placed in the tray information portion.

    f. Press Esc once to return to menu.

16. Put tray with samples in appropriate cup locations on autosampler. Position try to the cup containing standard A (usually #35 or so). Select "Start Analysis." Press <enter>.

17. The second screen will ask if the tray has standards or not. If you standardized the first tray of the run and all the check standards are within QC ranges, recalibration for the next tray is <u>not</u> necessary. Select appropriate option. Press <enter>.

18. Press Alt, Esc keys together, to get back to background to view the calibration peaks.

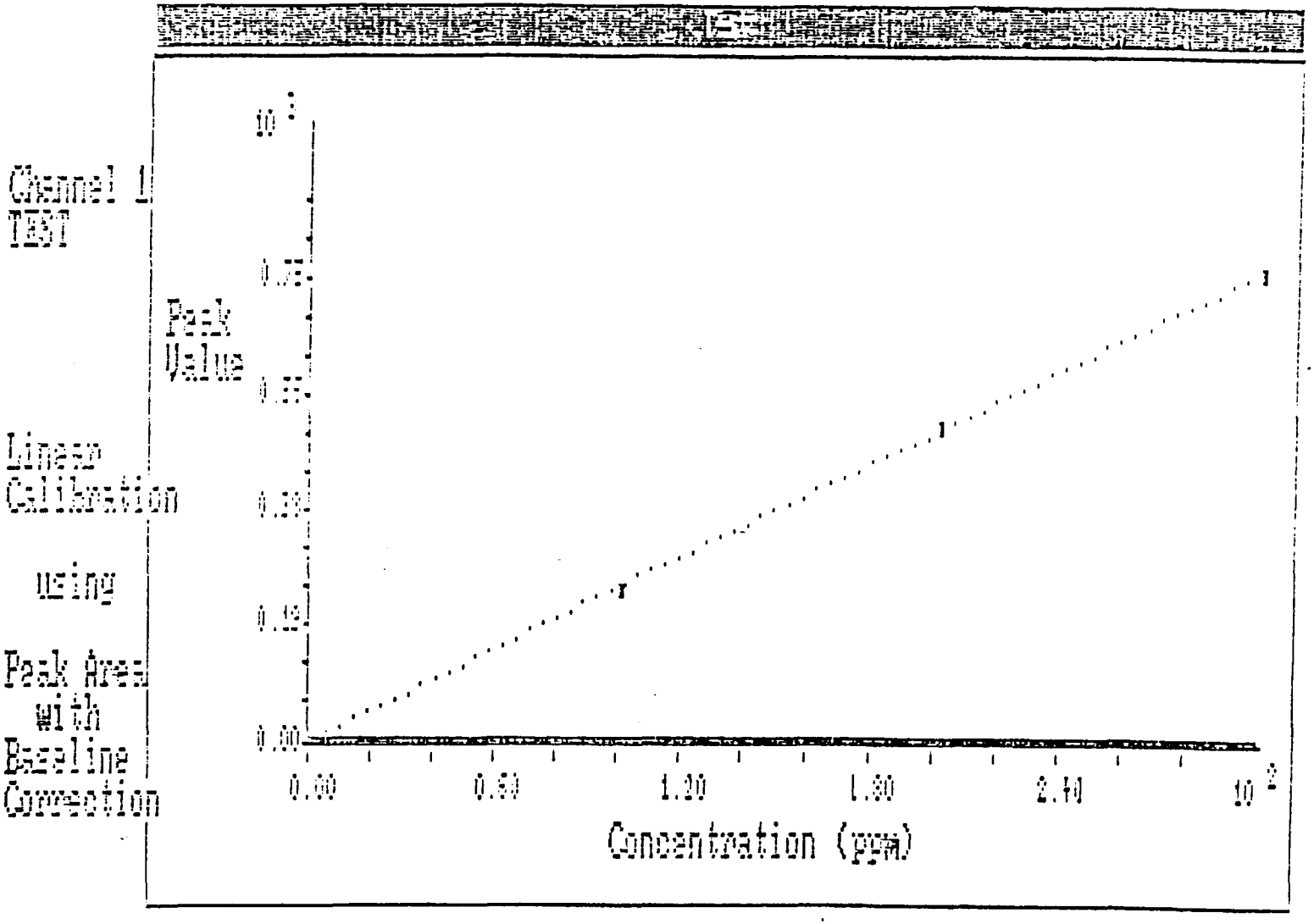
    After calibration is complete:

    - go into the foreground (Press Alt, Esc keys)
    - select "display calibration graph" (Press <enter>)
    - review the data
    - return to the background (Press Alt, Esc keys)

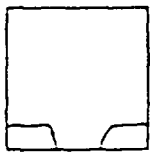
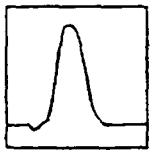
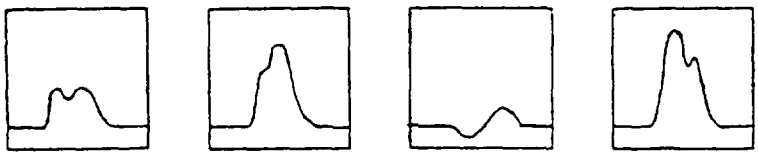
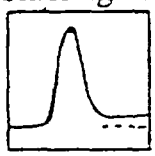
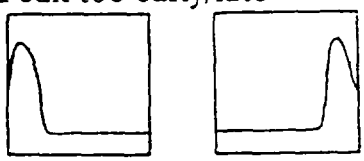
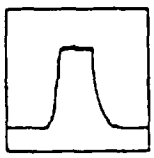
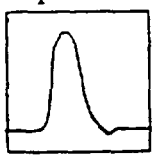
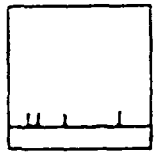
D. Quikchem Calibration

QuikCalc II uses a calibration technique called multisegment linear fitting which gives extensive flexibility to the user. It allows the calibration curve to be defined in terms of individual linear segments which can span each of several standards. Following processing of the calibration standards, a correlation coefficient is calculated for each segment with more than two standards or replicates. It provides important statistical information about each segment and gives the user a high degree of confidence in the determined sample values. See Figure 1.

Calibration
FIGURE 1



Correlation Coefficient: 0.99925 Press the [Esc] key to continue.

Problem:	Cause:
Negative peak 	1. Contaminated carrier 2. Bad or no SO_4 column or sample extremely high in hardness 3. Samples high in oxidizing agents
Reproduceable dip when valve switches (before peak) 	1. Bad color reagent 2. Could also be valve turning artifact caused by a highly colored reagent
Odd looking peaks 	1. Index of refraction problem, matrix related (usually acid or pH buffering) 2. Also method interferences: high hardness on SO_4 method, oxidizing samples on nitrate method 3. Bad reagents
Shifting baseline 	1. Flow problem 2. Precipitate build-up on SO_4 manifold tubing
Peak too early/late 	1. Usually flow problem 2. Valve not set to an initial load position state before starting run 3. Incorrect pump setting or other timing problem
Peak cut off **in** window 	1. Reagents exceeded-reagents improperly prepared 2. Standards incorrectly prepared
Reproduceable dip after peak 	1. Bad column
Small intermittent peaks 	1. Milli-Q or reagents not degassed properly or adequately 2. Waste line coil not installed (for the methods which require it)

Three basic areas of troubleshooting:

1. Fluidics (clogs, old pump tubing, crimp in manifold tubing)
2. Chemistry
3. Timing (not usually a problem after initial development)

BLH/rff
[rff-genpol-604]

APPENDIX B-9

TOTAL ORGANIC CARBON - WATER (WARZYN)

Effective: 8-24-1

TOTAL ORGANIC CARBON

Scope and Application: This method is applicable to surface water, sewage, wastewater and groundwater.

Method: Each standard and sample is sealed in an ampule containing sodium persulfate and phosphoric acid. The ampules are heated for 2 hours at 95°C. The oxidized organic carbon is measured as CO_2 by infra-red detection. Quantitation is determined using an external standard curve.

Reference: EPA 1983: method 415.1, OI Model 524C Total Carbon System Manual

Detection Limit: 1.0 mg/L

Optimum Range: 1.0 - 20 mg/L

Sample Handling: Acidify with concentrated sulfuric acid to pH <2 and refrigerate at 4°C. Analyze within 28 days.

Reagents and Apparatus:

1. OI Model 524C Total Carbon System
2. 10 mL sealed ampules (OI Corp.)
3. Commercial grade O_2 gas
4. Disposable propane gas cylinder
5. Commercial-grade N_2 gas (high purity, dry grade)
6. Eppendorf microliter pipet, 100-1000 uL
7. Oxford macropipet, 0-5 mL
8. Silicone grease
9. Saturated potassium persulfate solution
10. Phosphoric acid solution, 10% v/v
11. Milli-Q water
12. Potassium biphthalate (KHP)
13. Volumetric flasks, 1000 mL and 100 mL
14. Pipets, 1-20 mL assorted
15. EPA quality control sample of known concentration.

Reagent Preparation: (Prepare fresh every six months, unless otherwise stated).

1. **Total Organic Carbon (TOC) Stock Solution, 1000 mg/L:** Dry potassium biphthalate (KHP) at 105°C for 2 hours. Cool in a desiccator. Weigh exactly 2.1254 g dry KHP and add to a 1000 mL volumetric flask containing 2 mL of concentrated H2S04 and Milli-Q water. Mix well and dilute to the mark. Store in refrigerator.

2. **Intermediate TOC Solution (100 ug/mL):** To a 100 mL volumetric flask, pipet 10.0 mL of the 1000 mg/L stock solution. Dilute to the mark with Milli-Q water. **Prepare fresh monthly.**

3. **Standard Carbon Solutions:** (Prepare fresh for each run.)

   20 mg/L TOC Standard: To a 100 mL volumetric flask, pipet 20.0 mL of the 100 mg/L carbon solution, and dilute to the mark with Milli-Q water.

   10 mg/L TOC Standard: To a 100 mL volumetric flask, pipet 10.0 mL of the 100 mg/L carbon solution, and dilute to the mark with Milli-Q water.

   5 mg/L TOC Standard: To a 100 mL volumetric flask, pipet 5.0 mL of the 100 mg/L carbon solution, and dilute to the mark with Milli-Q water.

   3 mg/L TOC Standard: To a 100 mL volumetric flask, pipet 3.0 mL of the 100 mg/L carbon solution, and dilute to the mark with Milli-Q water.

   1 mg/L TOC Standard: To a 100 mL volumetric flask, pipet 1.0 mL of the 100 mg/L solution, and dilute to the mark with Milli-Q water.

4. **Potassium Persulfate Solution ($K_2S_2O_8$), Saturated:** Fill a 1-liter amber glass bottle 3/4 full with Milli-Q water. Add potassium persulfate , approximately 20 g, until no more crystals will dissolve. Store in refrigerator.

5. **Phosphoric acid solution, 10% (v/v):** Slowly add 100 mL of phosphoric acid to 900 mL Milli-Q water on a stirring plate. Mix thoroughly. Store in refrigerator.

Ampule Preparation:

1. Set up run by labeling ampules and placing them in a test tube rack.

2. Snap the ampules open along scoring and replace into rack in run sequence. Discard ampule tips. Keep open ampules covered with aluminum foil to protect from dust and other contaminants.

3. Using an Eppendorf 1000 microliter pipet, carefully pipet 1000 ul of saturated potassium persulfate solution into each ampule.

4. Using a calibrated Oxford Macropipet, carefully pipet 5.0 ml of standard or sample into each ampule. For blanks, pipet 5.0 ml Milli-Q water. For spiked samples pipet 4 ml of sample and 1 ml of the 20 mg/L standard into an ampule.

5. Using Eppendorf microliter pipet, carefully pipet 300 ul of 10% phosphoric acid solution into each ampule.

Ampule Purging and Sealing Procedure:

1. Open oxygen and propane cylinder main valves.

2. Open propane toggle switch and purge propane line for a couple seconds by opening propane adjust valve; then close valve.

3. Light burner while slowly opening propane adjust valve until a flame approximately 2 inches high is obtained.

4. Open oxygen toggle switch. Open oxygen adjust valve slowly until **each** flame has a blue cone in the center.

5. Place 8 ampules in purging rack. Rinse purge tubes with Milli-Q water and insert tubes to the bottom of each ampule.

6. Purge ampules with oxygen for 6 minutes.

7. Place an ampule (purged for 6 minutes) into clamping assembly.

8. Swing microburner into place around ampule tip and seal.

9. Swing microburner back as soon as ampule is sealed.

10. Remove sealed ampule and replace into test tube rack. Open clamping assembly and drop hot ampule tip into a beaker partially filled with water.

11. Rinse purge tube. Place another ampule on purging rack and insert purge tube.

12. Continue with steps 4-8 for remaining ampules.

13. Turn off oxygen and propane main cylinder valves.

14. Place rack of sealed ampules in a 95°C oven for 2 hours. Cool to room temperature.

Analysis Procedure:

1. IR power should be on at all times.
2. Change primary drying tube desiccant (magnesium perchlorate).
3. Open nitrogen cylinder main valve.

4. Analyze ampules.

   4.1 Turn integrator power on.
   4.2 Place plastic stress adapter and gum rubber seal on neck of first ampule to be read. Silicone grease may be necessary to slide the seal over ampule tip.
   4.3 Place ampule in breaking assembly and turn clamping screw until ampule is sealed firmly in place.
   4.4 Lower purge tube until it is level with the tip of the ampule.
   4.5 Open zero gas valve (nitrogen). Adjust flow to 13 on the flowmeter (200 ml/min). Purge the airspace around ampule tip until IR meter needle returns to zero. For first ampule only, push auto zero button to zero instrument. Clear integrator display.
   4.6 Close zero gas valve.
   4.7 Raise purge tube above plunger/cutter edges.
   4.8 Lower plunger/cutter with a twisting motion, breaking ampule tip.
   4.9 Lower purge tube to within 1/8" of ampule bottom.
   4.10 Open zero gas valve. Make sure flowrate stabilizes at 13. Purge ampule until integrator stops. Record integrator reading on TOC data sheet.

4.11 Close zero gas valve.
4.12 Remove ampule and discard. Analyze each ampule according to steps 4.2 - 4.12.

5. Instrument shut-down.

   5.1 Turn off integrator.
   5.2 Close nitrogen cylinder main valve.
   5.3 Clean and lubricate plunger/cutter and barrel assembly.
   5.4 Leave IR power on.

Quality Control:

1. A standard curve consisting of a 20 mg/L, 10 mg/L, 5 mg/L, 3mg/L and 1 mg/L should be analyzed in duplicate. A check standard at 10 mg/L should be analyzed immediately prior to the first sample, every eleventh analysis thereafter and at the end of a run. Recovery of the check standard should be 90% - 110%. If a recovery is outside the Q.C. limits, all samples must be reanalyzed back to the last acceptable check standard.

2. A blank must be analyzed after every check standard.

3. An EPA quality control sample should be analyzed immediately after the initial check standard and blank. Results should be within 80-120% and the 95% confidence limits, or samples must be reanalyzed.

4. A duplicate should be analyzed with each set of 10 samples. Calculate RPD and record to 1 decimal point on data sheet. Recovery should be within acceptable limits, or data must be flagged appropriately.

5. A spike should be analyzed with each set of 10 samples. If less than 10 samples are analyzed a spike is still required. Recovery should be within acceptable limits, or data must be flagged appropriately.

6. If any instrument reading is above the range of the standards, the sample must be diluted and repeated. The diluted level must be between 3 mg/L and 20 mg/L or redilute at a level that is within this range and reanalyze.

7. All reagent preparation as well as sample dilutions, and spikes should be documented in a logbook.

Calculations:

1. **Standardization:** Average responses for duplicate curves. Plot concentration vs. integrator response on graph paper.

2. Derive samples concentrations from graph as appropriate. Report results to 1 place past the decimal point from 1 to 99.9 and to 3 significant figures above 100.

Effective: 3-2-91

TOTAL ORGANIC CARBON INSTRUMENT OPERATING PROCEDURE

Scope and Application: This instrument operating procedure (IOP) covers the general daily use and maintenance of the Model 524C Carbon Analyzer. Set-up, troubleshooting, and more detailed information can be found in the instrument manual.

Instrument: O.I. Corporation Model 524C-ATO Carbon Analyzer
Purging and Sealing Unit
Analyzer Module

Materials: Milli-Q Water
Disposable Propane Cylinder
Oxygen Cylinder
Nitrogen Cylinder
CO2 Calibration Cylinder

Purging and Sealing Procedure:

1. Open main valves on the propane and oxygen cylinders (20 psi delivery).
2. Open propane toggle switch and purge propane line for a couple seconds by opening propane adjust valve; then close valve.
3. Light burner while slowly opening propane adjust valve until a flame approximately 2 inches high is obtained.
4. Open oxygen toggle switch. Open oxygen adjust valve slowly until **each** flame has a blue cone in the center.
5. Place 8 ampules in purging rack. Rinse purge tubes with Milli-Q water and insert tubes to the bottom of each ampule.
6. Purge ampules with oxygen for 6 minutes.
7. Place an ampule (purged for 6 minutes) into clamping assembly.
8. Swing microburner into place around ampule tip and seal.
9. Swing microburner back as soon as ampule is sealed.
10. Remove sealed ampule and replace into test tube rack. Open clamping assembly and drop hot ampule tip into a beaker partially filled with water.
11. Rinse purge tube. Place another ampule on purging rack and insert purge tube.
12. Continue with steps 7-11 for remaining ampules. Turn off oxygen and propane main cylinder valves. Place rack of sealed ampules in a 95°C oven for 2 hours. Cool to room temperature.

Analyzing Procedure:

1. IR power should be left on at all times.

2. Change primary drying tube desiccant (magnesium perchlorate).

3. Open nitrogen cylinder main valve.

4. **Zero integrator:**

   4.1 Turn integrator power on.

   4.2 Place plastic stress adapter and gum rubber seal on neck of a sealed ampule. (Silicone grease may be necessary to easily slide the seal over ampule tip).

   4.3 Place ampule in breaking assembly and turn clamping screw until ampule is sealed firmly in place.

   4.4 Lower purge tube until it is level with tip of the ampule.

   4.5 Open zero gas valve (nitrogen). Adjust flow to 13 on the flowmeter (200 ml/min). Purge the airspace around ampule tip until IR meter needle returns to zero. Push auto zero button and clear integrator display.

   4.6 Close zero gas valve. Unscrew clamp and remove ampule.

5. **Analyze ampules in following order:** standard curve (high to low), check standard, reagent blank, EPA QC sample, and then samples. Analyze one spike, one duplicate and one continuing calibration standard for every 10 samples. End run with a continuing calibration standard.

   5.1 Place adapter and gum rubber seal over neck of ampule to be analyzed.

   5.2 Place ampule in breaking assembly and turn clamping screw until ampule is sealed firmly in place.

   5.3 Lower purge tube until even with the tip of the ampule.

   5.4 Open zero gas valve. Purge airspace around ampule tip until integrator stops. Clear integrator display. Close zero gas valve.

   5.5 Raise purge tube above plunger/cutter edges.

   5.6 Lower plunger/cutter with a twisting motion, breaking ampule tip.

   5.7 Lower purge tube to within 1/8" of ampule bottom.

   5.8 Open zero gas valve. Make sure flowrate stabilizes at 13. Purge ampule until integrator stops. Record integrator reading on TOC data sheet. Clear display.

5.9 Close zero gas valve.

5.10 Remove ampule and discard. Analyze each ampule according to steps 5.1 - 5.9.

6. **Instrument shut-down.**

   6.1 Turn off integrator.

   6.2 Close nitrogen cylinder main valve.

   6.3 Clean and lubricate plunger/cutter and barrel assembly.

   6.4 Leave IR power on.

Zero and span settings should be checked monthly:

Procedure:

1. Open main valves on nitrogen and CO2 calibration cylinders.
2. Clamp ampule into breaking assembly.
3. Open zero gas toggle switch and allow system to purge at a flow rate of 13.
4. Zero IR meter needle by adjusting zero control knob until the needle reads exactly zero. Close zero gas toggle switch.
5. Open span gas toggle switch and allow system to purge at a flow rate of 13 until IR meter reaches a maximum.
6. Adjust span control knob until the IR meter gives a reading matching the calibration curve value for the span gas CO2 concentration.
7. Turn span gas off and zero gas on using toggle switches. Allow meter to stabilize and, if necessary, adjust the zero control knob so that the meter reads exactly zero.
8. Switch zero gas off and span gas on. The meter should return to the previously set reading. Adjust span control knob if necessary.
9. Continue making small zero and span adjustments until the IR meter reaches the zero and span settings without adjustment when the gases are alternated.
10. Document zero and span adjustment in TOC Analyzer logbook.

APPENDIX B-10

TOTAL ORGANIC CARBON - SOIL (ETC)

TITLE: Method for the Determination of Total Carbon and Total Organic Carbon in Sediment, Sludge and Soil Samples Approval: Lab Manager Review: QA Manager	Doc.#ED522903 Revision #3 Effective Date 12/11/92

1.0 METHOD SUMMARY

1.1 Total Organic Carbon is measured using the Dohrman DC-80 carbon analyzer coupled with the PRG-1 furnace module.

1.2 A known weight of sample is combusted in an oxygen atmosphere at 800°C, in the presence of a copper catalyst. Carbonaceous materials are converted to carbon dioxide. The CO_2 formed is quantified using an NDIR detector.

1.3 Intact samples are taken for analysis to minimize loss of volatile components.

1.4 Data is reported in mg/kg. Method detection limit is 100 mg/kg.

1.5 If the results are to be reported on a "dry weight basis", a separate % solids determination is required and is applied to data calculations.

2.0 APPARATUS

2.1 Dohrman DC-80 Carbon Analyzer

2.2 Dohrman PRG-1 Furnace Module

2.3 Dohrman Sludge/Sediment Sampler Accessory

2.4 50 ul syringe (unimetrics)

2.5 Chann Electro Balance

2.6 Quartz Wool and Sample Boats

2.7 Stainless Steel Forcepts/Spatula

2.8 Dohrmann Oxidation Promotor (PN 511-883)

3.0 REAGENTS

3.1 Carbon stock solution (10,000 mg/l) - dissolve 21.2800 grams of primary standard grade potassium hydrogen phthalate (anhydrous, dried at 105°C for 2 hours, cooled in a dessicator) into 800 ml of DIHOH (1 ml = 10.0 mg). Add 2 ml 1+1 H_2SO_4, then dilute to 1 litre with DIHOH. Stock solution is stable for 6 months.

3.2 4000 mg/l standard - dilute 40 ml of the "stock" solution. Add 2 ml of 1+1 H_2SO_4, then dilute to 100 ml.

3.3 2000 mg/l standard - dilute 20 ml of the "stock" solution. Add 2 ml of 1+1 H_2SO_4, then dilute to 100 ml.

3.4 1000 mg/l standard - dilute 10 ml of the "stock" solution. Add 2 ml 1+1 H_2SO_4, then dilute to 100 ml.

3.5 100 mg/l standard - dilute 1.0 ml of the "stock" solution. Add 2 ml of 1+1 H_2SO_4, then dilute to 100 ml.

3.6 Standards for soil analysis must be prepared fresh weekly.

3.7 H_2SO_4 solution (1+1) (V/V) - Add with constant mixing in an ice bath. 100 ml of concentrated ACS AR grade sulfuric acid to 100 ml of deionized water.

3.8 Potassium persulfate - phosphoric acid reagent (2%). Dissolve 20.0 g of reagent grade potassium persulfate (K_2S_{208}), add 2.0 ml of concentrated (85%) phosphoric acid (H_2PO_4). Mix thoroughly and dilute to 1 litre with DIHOH. Prepare fresh monthly.

3.9 Hydrochloric acid solution (1+9) - add 10 ml of conc. ACS (AR) HCL to 90 ml of DIHOH. Mix thoroughly.

4.0 INTERFERENCES

4.1 Inorganic carbon (carbonates and bi-carbonates) represent positi interferences. Inorganic carbon is removed by treating a known weight of sample with several drops of 1+9 HCL solution. Additional acid is added dropwise until inorganic carbonate removal is complete.

4.2 Non-homogenous matrices may yield poor reproducibility. Homogenize the intact sample by grinding to obtain a representative aliquot.

5.0 ELECTRO BALANCE CALIBRATION

5.1 Check and document the calibration of the electro balance as per the instrument manual.

5.2 Identical weighing pans should be in place on the "B" and "tare" positions of the balance.

5.3 Set the range at the "B" 1200 mg position. The readout should be 0.00 mg. Close the balance. Allow to stabilize, then depress the tare. The readout should be stable at 0.00 mg.

5.4 Place a 1000 mg Class "S" weight on the Pan "B". Record the result. Depress the "CAL" button to calculate to 1000 mg. Record the result. Repeat the procedure and confirm calibration.

5.5 Then weigh and record the values obtained from the following Class "S" weights:

100.0 mg
10.0 mg
5.0 mg

5.6 All values obtained should be within 1% of the expected value. If not, recalibrate the balance as per Section 5.0.

6.0 CARBON ANALYZER - PRELIMINARY SET UP FOR SOIL ANALYSIS

6.1 Check all instrument components as per the Dohrman DC-80 instrument manual. Furnace inlet tube to bulkhead #5, furnace outlet tube is connected to bulkhead #4. Also see attached assembly drawing.

6.2 Position the boat carriage under the sample inlet block. Place the sample boat into the carrier using forcepts. Place a piece of quartz wool into the boat and close the inlet block.

6.3 Turn on the power to the PRG-1 furnace module.

6.4 If fresh oxidation promotor (PN 511-883) is used, condition by heating for 1 hour with the furnace exit tube immersed in basic DIHOH. After 1 hour, connect the furnace exit tube to the UV module at bulkhead #4. Verify flow within the reactor.

6.5 If "pre-conditioned" oxidation promotor is used, connect the furnace exit tube to the UV reactor module at bulkhead #4. Verify flow within the reactor. Allow the system to come to full temperature and stabilize for 30 minutes.

6.6 Verify the following:

- Oxygen is flowing in the reactor
- Normal system back pressure
- UV lamp is turned off
- Reactor is filled with reagent
- Quartz wool is in the boat
- Mode is TOC
- Volume is 40 ml
- Pump is on
- Baseline is stable at 0.0100 units in "DET" mode

6.7 Set the IR mode to DET. Decalibrate the instrument by depressing the CALIB button for 3 seconds.

6.8 Adjust the baseline to 0.0100 units. It should be stable after the furnace temperature has reached 800°C ± 0.002 units.

6.9 Decontaminate the sample boat by pushing it into the combustion zone for 2 minutes. This will remove any organic residues on the boat. Instrument baseline will return to normal when boat is clean.

7.0 CALIBRATION

7.1 Inject 40 ul of the 2000.0 mg/l carbon standard into the cool sample boat via the liquid injection port. Slide the boat into the combustion zone.

7.2 Depress the start button. Then on completion of the cycle, record the PPM response obtained on the LED. Bring the boat out of the furnace into the inlet block and allow to cool. Inject three additional 40 ul volumes on the 2000 mg/l calibration standard. The response values should be within 5% of the mean. If not, repeat the calibration procedure.

7.3 Press the "calibrate" button and record the mean response value and the "adjusted" PPM value from the calibration sequence. The value should be 2000.0 PPM C ± 5%.

8.0 CHECK STANDARD ANALYSIS

8.1 Analyze single 40 ul injections of each of the following acidifi and sparged standard solutions.

Method Blank

100 mg/l carbon standard
1000 mg/l carbon standard
2000 mg/l carbon standard
4000 mg/l carbon standard

8.2 Calculate the % Recovery. Recoveries should be within 10% of the known standard value. If not, re-analyze the standard.

$$\% \text{ Rec} = \frac{\text{Observed Result}}{\text{Known Result}} \times 100$$

9.0 SAMPLE ANALYSIS

9.1 Remove the quartz wool and tare the cool, clean sample boat on pan "B" (1200 mg range) of the electro balance. Remove the tared boat from the balance, then add a homogenous amount of sample to the boat. Reweigh and record the weight in mg.

9.1.1 If organic carbon is to be determined, remove inorganic carbonates by treating a known weight of sample with several drops of 1+9 HCL. Wait until effervescing is completed and add additional acid. Continue this process until the incremental addition of acid causes no further effervescence. Proceed to 9.3.

9.2 If total carbon is to be determined, omit the addition of HCL reagent to the sample. Report data as "Total Carbon". Proceed to 9.3.

9.3 Transfer the "loaded boat" to the sample carriage via the inlet block. Allow the system to stabilize for 30 seconds after closing the inlet block.

9.4 Push the start button and slide the boat into the furnace combustion zone. Allow the instrument to complete the cycle. Record the PPM value obtained from the LED display.

9.5 Analyze all samples in duplicate.

9.6 Calculate the carbon concentration for the sample using the following:

$$mg/kg = \frac{40 \text{ (LED ppm)}}{\text{Sample weight mg (corrected for \% solids)}}$$

10.0 QUALITY CONTROL

10.1 Four calibration standards are analyzed for each analytical run. The recoveries for the standards must be within +/- 10% with the exception of the low standard which must be +/- 15%.

10.2 A 2000 PPM calibration check standard is analyzed every 10 samples and at the end of each analytical run. The recovery must be within +/- 15%.

10.3 A method blank is analyzed once per 20 samples. Results for the blank must be less than the MDL.

10.4 An EPA reference QC sample is analyzed for each batch and the recovery must be within +/- 20% of the known value.

10.5 A duplicate analysis is performed at a frequency of 1 per 10 samples. Duplicate relative percent difference should be:

+/- 20 at > 5 times the MDL
+/- MDL at < 5 times the MDL to = MDL
NC at < MDL

11.0 REPORTING REQUIREMENTS

11.1 All results are reported in mg/kg on a dry weight basis. The minimum reporting level is 100 mg/kg.

11.2 All results are reported to three significant figures.

11.3 Values below the MDL are reported at < "MDL".

12.0 REFERENCES

12.1 Method 415.1, Methods for Chemical Analysis of Water and Waste, E[illegible] 6004-79-020.

12.2 Method 9060, Test Methods for Evaluating Solid Wastes, SW-846 Third Edition.

12.3 Determination of Total Organic Carbon in Soil and Sediment, EPA AD/A103 788, Section 3-73.

APPENDIX B-11

LOW LEVEL METALS (WARZYN)

Effective: 7-2-91

ACID DIGESTION FOR AQUEOUS SAMPLES AND EXTRACTS
ICP/Flame-AA

Scope and Application: This acid digestion is applicable to all aqueous sample matrices. A nitric/hydrochloric acid digestion is used to prepare all samples which are to be analyzed by flame atomic absorption spectroscopy (flame-AA) or by inductively coupled plasma spectroscopy (ICP). A nitric acid/hydrogen peroxide digestion is used to prepare samples for analysis by graphite furnace atomic absorption spectroscopy (GFAA).

Method: Nitric acid/hydrogen peroxide and nitric/hydrochloric acid digestions

Reference: "Statement of Work for Inorganic Analysis", ILM01.0, EPA 1990

Sample Handling: Aqueous samples must be acidified with concentrated nitric acid to pH <2. Set up digestion as soon as possible; digested sample must be analyzed within 6 months.

Reagents and Apparatus:

1. Hot plate
2. 250 mL beakers
3. 100 mL graduated cylinders
4. Class A volumetric glassware
5. Deionized (D.I.) water
6. Instra-analyzed nitric acid, or equivalent
7. Distilled nitric acid (GFAA digestion only)
8. Instra-analyzed HCl acid, or equivalent
9. Stock and standard metal solutions
10. Whatman #42 filter paper
11. Glass or plastic funnels
12. Watch glasses
13. 30% Hydrogen peroxide

Reagent Preparation:

1. **Intermediate and working metal solutions:** Refer to the specific metal SOP for instructions on preparation.

2. **1:1 Hydrochloric acid (HCl):** Using a graduated cylinder, add 250 mL D.I. water to a to a 500 mL (or 1 L) repipettor. Carefully add 250 mL of concentrated HCl and mix.

3. **1:1 Nitric acid (HNO_3):** Using a graduated cylinder, add 250 mL D.I. water to a to a 500 mL (or 1 L) repipettor. Carefully add 250 mL of concentrated HNO_3 and mix.

Notes:

1. A separate digestion is required for mercury analyzed by the AA-Cold Vapor technique. (See "Mercury Digestion-Aqueous Samples")

2. All samples, duplicates, and spikes, as well as any required prep or digested blanks and standards, must be carried through the digestion procedure.

3. If samples boil or go to dryness (**any** dry spots on the bottom of the beaker) at any time during the digestion, some of the analyte may have been lost. The digestion must be discarded and the affected samples must be reprepared.

4. If elevated analyte levels are expected, the spike concentration may be increased accordingly.

Procedure:

Digestion Procedure for Flame-AA and ICP:

1. All glassware must be acid-washed with 1:1 nitric acid and thoroughly rinsed with D.I. water prior to use.

2. Measure out 100 mL aliquots of samples, blanks, and standards into 250 mL beakers using a graduated cylinder.

3. Add 2.0 mL of 1:1 HNO_3 and 10 mL of 1:1 HCl.

4. Cover with a watch glass and heat on the hot plate for 2 hours or until the volume has been reduced to between 25 and 50 mL. Adjust the temperature of the hot plate as needed to prevent samples from boiling.

5. Allow samples to cool. If any insoluble material remains, filter samples through Whatman #42 filters. Quantitatively transfer digested samples, blanks, and standards into 100 mL volumetric flasks. Rinse beakers and filters with D.I. water and dilute to volume to 100 mL.

6. Samples are now ready for analysis using the AA-flame or ICP methods.

Digestion Procedure for GFAA:

1. All glassware must be acid-washed with 1:1 nitric acid and thoroughly rinsed with D.I. water prior to use.

2. Measure out 100 mL aliquots of samples, blanks, and standards into 250 mL beakers using a graduated cylinder.

3. Add 1.0 mL of 1:1 HNO_3 and 2.0 mL of 30% H_2O_2.

4. Cover with a watch glass and heat on the hot plate for 2 hours or until the volume has been reduced to between 25 and 50 mL. Adjust the temperature of the hot plate as needed to prevent samples from boiling.

5. Allow samples to cool. If any insoluble material remains, filter samples through Whatman #42 filters. Quantitatively transfer digested samples, blanks, and standards into 100 mL volumetric flasks. Rinse beakers and filters with D.I. water and dilute to volume to 100 mL.

6. Samples are now ready for GFAA analysis.

Quality Control:

1. A digested blank and standard (spiked blank) must be included with each batch of samples that is digested. The blank is a check for possible contamination during the digestion process; the standard is a check for possible analyte loss during digestion.

2. A matrix spike and duplicate must be prepared, at a minimum, for every 10 samples digested. If fewer than 10 samples are digested a spike and duplicate are still required.

Effective: 5-3-91

INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROMETRIC METHOD

Scope and Application: Metals in solution can be readily analyzed by atomic emission using an inductively coupled plasma. Dissolved metals are determined in filtered and acidified samples. Total metals are determined in acidified, but unfiltered samples. Appropriate steps must be taken in all analyses to ensure that potential spectral interferences are taken into account.

Method: Inductively coupled plasma - atomic emission.

Reference: "Methods for Chemical Analysis of Water and Wastes", Method 200.7 EPA 1984.

"Inductively Coupled Plasma - Atomic Emission Spectroscopy", Method 6010, SW-846, November 1986.

"Statement of Work for Inorganic Analysis", ILM01.0, EPA 1990

"Instructions: Plasma 40 Emission Spectrometer", Perkin-Elmer, 1987.

Sample Handling: Acidify aqueous samples with concentrated nitric acid to pH <2. All samples must be digested prior to analysis (refer to appropriate digestion procedure). All samples must be analyzed within 6 months of sampling date.

Reagents and Appartus:

1. Plasma 40 Perkin-Elmer ICP Spectrometer
2. Argon (liquid: "high purity" or gaseous: "prepurified" grade)
3. Stock and intermediate metal standard solutions
4. EPA, ERA, or other reference standard solutions
5. Nitric acid, conc. (instra-analyzed or equivalent grade)
6. Class A volumetric glassware
7. Deionized water
8. Disposable 15 mL centrifuge tubes
9. 100 uL Eppendorf pipetter
10. 5 or 10 mL Oxford pipetter
11. Yttrium or Scandium stock solution
12. IBM AT Computer or equivalent
13. Epson 800 printer

Procedure:

Instrument Set-Up Procedure for Plasma 40:

1. Turn ON power switch if necessary (routinely left ON throughout week). Allow 1 hour for RF generator to warm up and electronic and optical components to achieve thermal equilibrium.

2. Perform daily maintenance as specified in Maintenance Procedures: check pump, pump tubing, and nebulizer tips for wear, cleanliness, etc.

3. Turn on argon at tank. The first three indicator lights on the ICP (Power, RF ready, Interlock) should light.

4. Lock pump tubing in place, raise torch to the "ignite" position, and press "RF on".

5. When plasma ignites, lower torch to the run position (the injector tip should be even with or just below the bottom of the lowest RF coil).

6. Turn on pump and aspirate rinse water*. Allow plasma to stabilize 30 to 40 minutes before starting analysis.

Computer Start-Up Procedure:

1. Turn computer and printer power on (the computer will automatically start with a memory check).

2. Type CD ICP and press Return to enter the ICP directory. Then type ICP and press Return again to load software (approximately 10-15 seconds).

3. Perform a BEC check as specified in Maintenance Procedures. The BEC and CV values must be within the specified range before any analysis is done.

Sample Analysis:

1. Before starting analysis, for each element to be analyzed:

   a. Press F1 to select the Element mode, type the appropriate element file name and press Alt F9 to retrieve it from Library.

   b. Press F8 to select Spectrum mode.

   c. Analyze a single element standard at approximately 2-10X the IDL.

   d. Analyze the ICS AB solution.

   e. Analyze 1-3 samples representative of the digestion set.

   f. Compare the displayed spectra to check for spectral interferences. Reset background correction points as needed. If there are overlapping peaks or other spectral interferences present, an alternate wavelength or interelement correction must be used.

   g. Press F8 to leave the Spectrum mode. If wavelength calibration or background correction points were changed, press F9 to save the changes.

* Rinse water should be D.I. water with a small amount of liquid detergent (such as Liquinox or Whisk) added to improve wetting of tubing and spray chamber. Approximately 1-2 mL of soap per 500 mL water should be sufficient.

2. To store a list of sample labels to be used for the analytical run, select Report mode (F3), then ID/Wt mode (F8). Enter a file name, type in N (no) in the field for raw emission counts, mg/L for uncorrected units, and leave the corrected units field blank. Enter sample labels in the sample ID field in the exact order of analysis; include all check standards, QC samples, etc. If it is possible that additional samples may be added to the end of an analytical run (dilutions, post-digestion spikes, linear range standards, etc.) add additional sample labels to the ID/Wt file in the form of single letters (A, B, C, etc.) and manually write in the correct sample labels after the analytical run is completed. Alternatively, a new ID/Wt file may be created **after** the analytical run is completed (in this case the raw data must be reprinted with the new file by selecting Report Format 1 (F5) in the report mode and responding to the prompts). Save ID/Wt files by pressing F9 (to library).

3. Press F2 to select the Method mode.

4. Type the method file name and press Alt F9 to retrieve the desired method panel from Library, or create a new panel using existing element files. Standard conditions are 35 second read delay, 2 replicates per sample, report format #2 and a data file name composed of the date (mmdd) and a sequential letter identifier (e.g. 0123B for the second analytical run on Jan 23). An internal standard (usually yttrium) must be included in any method. Background correction points are already included in each element file.

5. Add yttrium (or scandium) stock solution (1000 mg/L) as an internal standard to all standards, blanks, and samples in a ratio of 0.1 mL yttrium stock to 10 mL sample. This allows automatic correction for matrix differences in viscosity, surface tension, etc.. If the autosampler is to be used, samples can be pipetted directly into 15 mL centrifuge tubes. Otherwise mix sample and yttrium in small disposable beakers.

If autosampler is used:

1. If the autosampler is to be used, load sampler starting with the calibration standards in order of decreasing concentration (highest concentration first, calibration blank last).

2. Start automatic run (F5). Respond to the prompts that appear at the bottom of the screen:

   a. "Press start function key to begin this analysis": press F5

   b. "Enter ID/Wt file": type ID/Wt file name and press Return.

   c. "Do you wish to rinse between tubes (Y or N)": type Y and press Return. N may be selected only for clean samples where no carry-over problems are anticipated. **Always** rinse between samples when analysis is following CLP protocols, or analyzing for Sb, Cr, or Zn.

d. "Enter position of the last sample in tray": type appropriate number and press Return (you may wish to enter a number several positions past the last sample to allow room for the addition of necessary dilutions, etc. at the end of the run).

e. "Do you wish to re-standardize (Y or N)": type N or Y and press Return. N is usually selected. Y will allow restandardization of the instrument during an automatic run but additional autosampler positions will be unavailable for samples. If Y is selected, additional on-screen instructions will prompt for position of additional calibration standards.

f. "Do you wish to wavelength calibrate during the analysis? (Y or N)": type N or Y and press Return. N is usually selected. Y will allow recalibration of all wavelengths used in the current method before analysis is started but additional autosampler positions will be unavailable for samples. If Y is selected, additional on-screen instructions will prompt for position of additional wavelength calibration standards. The system will then begin the analysis.

3. When the analysis is complete press F2 to select Method mode before exiting software to ensure the data file is stored permanently. Then set up the next panel, return to Report mode to set up a new ID/Wt file or reprint data, or press ESC to exit the ICP software.

If samples are to be run manually:

1. Press F2 to start a manual run and respond to prompts to calibrate instrument: Press F6 (Standard), aspirate the first calibration standard and press Return. At the prompt, aspirate the next standard(s) and press Return. When all calibration standards have been analyzed press F5 (Blank) aspirate the calibration blank and press Return. This completes the instrument calibration.

2. To analyze samples, type in sample label if needed, press F7 (Sample), aspirate sample and press Return. Repeat with all samples in the run.

Computer Shut-Down Procedure:

1. When analysis is complete press F2 (Method mode). At the message "Do you wish to quit method"? Type Y.

2. Press "ESC". At the message "Do you wish to quit method?" Type Y.

3. Turn off computer power switch.

4. Turn off printer.

Caution: Never turn off computer power while still using ICP software. This can cause partial loss of files and other errors.

Instrument Shut-Down Procedure:

1. Aspirate a dilute nitric acid solution (approx. 10%) for 1 to 2 minutes to clean sample introduction system.

2. Aspirate D.I. water for 5 minutes to rinse system thoroughly.

3. Turn off pump and release pump tubing.

4. Press "RF off" to extinguish plasma.

5. Shut off argon flow at tank.

6. If the ICP **will not** be used for **2 days or more**, turn off ICP power switch. Otherwise, leave the ICP power **ON**.

Quality Control:

1. Establish a standard curve with the appropriate calibration standards plus a blank. Record the emission count for the internal standard in the ICP log book. The emission count should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check pump tubing, nebulizer tips, nebulizer flow, wavelength calibration, etc.).

2. **The first analyses for each analytical run are, in order:**

   a. Initial calibration verification standard (ICV)

   b. Initial calibration blank (ICB)

   c. Initial standard at 2X the CRDL (CRI). **Note:** The CRI is not necessary for Ca, Mg, Na or K.

   d. Initial interference check sample, solution A (ICSA).

   e. Initial interference check sample, solution AB (ICSAB)

   f. Laboratory control standard - an ERA, EPA, or other reference standard digested with the sample set (LCS)

To continue with sample analyses, the ICV must be within 90-110% of the true value, the ICB must be less than the CRDL, and the LCS and ICS solutions must be within 80-120% of the true value. If these QC criteria are not met, discontinue the analytical run and perform necessary troubleshooting.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are to be analyzed, a duplicate and spike are still required. Duplicates and spikes are to be within required control limits or the data must be flagged appropriately (N for spikes, * for duplicates). Additionally, if a digested spike is outside required control limits, a post-digestion spike must be analyzed for that sample.

4. For each sample batch (same matrix and project) one sample must be analyzed at an additional 5X dilution for the ICP serial dilution analysis (L). If the original sample concentration is at least 50X above the IDL, the serial dilution must agree within 10% of the original sample concentration or data for all associated samples must be flagged appropriately (E).

5. A continuing calibration verification standard (CCV) and blank (CCB) are to be analyzed, at a minimum, after every 10 analyses. If less than 10 analyses are performed, a CCV and CCB are still required. The last samples analyzed in the run are to be a CCV and CCB. The CCVs must be within 90 - 110% of the true value or the samples run after the last acceptable calibration standard are to be reanalyzed.

6. At the end of each analytical run, but before the final CCV and CCB, the CRI, and ICS solutions A and AB are to be reanalyzed. The ICS must be within 80-120% of the true value or the samples run after the last acceptable calibration verification standard are to be reanalyzed.

7. Refer to the appropriate Quality Assurance Project Plan (QAPP) for project specific QC information (additional QC requirements, matrix spike and duplicate control limits, etc.).

8. Detection limit verifications and linear range analyses must be performed each quarter. Interelement correction factors are to be determined annually at a minimum. Interelement correction factors must be recalculated on an analyte and wavelength specific basis any time background correction points are changed in an element file. Additionally, for greatest accuracy, interelement correction factors should be re-determined for any analytical batch that is expected to have high concentrations of common interferents (e.g. any soil, sediment, sludge, or leachate matrix).

Daily Maintenance Procedures - Plasma 40

1. **Pump rollers:** With the pump on, feel along the bottom of the pump to determine that all the rollers are turning smoothly with no resistance or pulling. If a "sticky" roller is found a service call must be placed to Perkin-Elmer to correct the problem. A sticky roller will cause rapid deterioration of pump tubing resulting in erratic results.

2. **Pump tubing:** Check pump tubing for excessive stretching, soft or flattened spots. This can cause irregular or diminished sample flow resulting in reduced sensitivity and lack of precision in sample results. When pump tubing is changed, (usually after 6-8 hours of use) it is necessary to trim ends of the new tubing so the length from the black stops to the end of the tubing is kept constant. Failure to trim tubing ends can cause imprecise results due to a longer sample read delay.

3. **Nebulizer tips:** Remove nebulizer end cap and check nebulizer tips visually and with the cleaning wire for clogs, salt build-up or other deposits. Follow the instructions in the Plasma 40 operating instructions for replacing nebulizer tips if necessary (Part 2, pg 3-8). Used tips may be cleaned by soaking overnight in 10% nitric acid followed by thorough rinsing with D.I. water. Finally, with the argon on, aspirate water and observe the spray pattern. The nebulizer should produce a fine, even mist with no large droplets with the direction of the spray approximately perpendicular to the face of the end cap (should not deviate more than about 20°). If the spray pattern looks uneven, "bent", or is pulsing excessively, recheck pump tubing and review nebulizer maintenance to correct the problem.

4. **BEC check:** This is an indication of how well the ICP system is performing. After the plasma has been ignited and allowed to stabilize for 30-40 minutes perform the following steps:

   a. At the DOS prompt type ICP and press Return to load software.

   b. Type MnBEC and press Alt F9 to retrieve this method from Library. Press F6 to start a manual run.

   c. Press F6 again (standards), aspirate a 1.0 mg/L Mn standard and press Return. The ICP will analyze 10 replicates of this standard. The Coefficient of Variance (CV) for these readings should be <2.0. If a higher values is obtained a sample introduction or instrument calibration problem is indicated. Check pump tubing and wavelength calibration for Mn and repeat the analysis. Record the CV in the maintenance log book.

   d. Press F5 (blank), aspirate a blank, and press Return to complete the calibration.

   f. Turn off the torch (RF off), aspirate D.I. water, and press F7 (sample). The resulting concentration should be $\leq |0.040|$. If a higher value is obtained, a problem with the sample introduction system is indicated. Review maintenance and, if the problem cannot be corrected, place a service call with Perkin-Elmer. Record the BEC in the maintenance log book.

   i. Re-light the torch and press ESC to end the manual run. Allow the plasma to stabilize 10-15 minutes before beginning any analysis.

5. **Final rinse:** When analysis for the day is complete, aspirate dilute (approx. 10%) nitric acid for one or two minutes followed by D.I. water for approximately 5 minutes. This will help prevent deposits from building up in the sample introduction system. Remember to release pump tubing when completed.

Weekly Computer Backup:

1. Once a week data files should be copied to floppy disks and deleted from the hard disk. Data files on floppy disks should be saved for one year.

2. Periodically (every 1-3 months depending on work volume), files should be reviewed, old files deleted and the entire system backed-up.

Other Maintenance:

1. Occasionally, additional maintenance will be necessary to correct problems arising from time and wear on the system. Any additional maintenance performed (including P.E. service calls) should be listed in the maintenance logs. These include periodic cleaning of the torch assembly, inspection of O-rings in torch assembly, and wavelength recalibration. Generally, these procedures will only be performed in response to observed problems. Refer to the Plasma 40 operating manual for specific directions.

ICAP CALIBRATION STANDARDS

Element	Wave-length	Detection Limit(ug/L)	Cal. Std. 1 (ug/L)	Cal. Std. 2 (ug/L)	Cal. Std. 3 (ug/L)	ICV (ug/L)	CCV (ug/L)
Al	237.335	50	20,000	400	---	2500	4000
Al	396.152	50	20,000	400	---	2500	4000
Sb	206.833	50	2000	500	250	1000	1000
Ba	233.527	10	10,000	200	---	500	2000
Be	313.107	5	1000	20	---	250	200
Cd	228.802	5	1000	50	---	500	200
Cd	214.438	5	1000	50	---	500	200
Ca	317.933	1000	200,000	10,000	---	10,000	80,000
Cr	267.716	10	10,000	500	200	1000	2000
Cr	205.552	10	10,000	500	200	1000	2000
Co	238.892	50	10,000	200	---	2500	2000
Co	228.616	10	10,000	200	---	2500	2000
Cu	324.754	10	10,000	100	---	1000	2000
Cu	224.700	20	10,000	100	---	1000	2000
Fe	238.204	20	20,000	200	---	1000	4000
Pb	220.353	100	10,000	500	---	5000	2000
Pb	216.999	100	10,000	500	---	5000	2000
Mg	285.213	1000	100,000	5000	---	10,000	40,000
Mn	257.610	10	10,000	100	---	500	2000
Ni	352.454	20	10,000	100	---	1000	2000
Ni	232.003	20	10,000	100	---	1000	2000
Ag	338.289	10	1000	---	50	500	200
Na	330.237	2000	100,000	5000	---	20,000	40,000
Sn	189.989	200	10,000	1000	---	2500	5000
V	292.402	50	10,000	500	250	2500	2000
Zn	213.856	10	10,000	100	50	500	2000

Forward copy to DM when revisions are made.

ICAP CALIBRATION STANDARDS

ICAP calibration standards are prepared from both multi-element stock solutions purchased from SPEX Industries (custom mixed standards) and single element stock solutions from VWR and Baxter (Ricca or Mallinckrodt as available).

XWE-1	XWE-2	XWE-3a	XWE-4a
2000 mg/L Fe	20,000 mg/L Ca	1000 mg/L Cr	2000 mg/L Al
1000 mg/L Cu	10,000 mg/L Mg	1000 mg/L Pb	1000 mg/L Ba
1000 mg/L Mn	10,000 mg/L Na	1000 mg/L V	1000 mg/L Co
1000 mg/L Ni		100 mg/L Cd	100 mg/L Be
1000 mg/L Zn			100 mg/L Ag

XWE-6a
500 mg/L Pb
250 mg/L Co, Al
100 mg/L Cu, Ni, Fe, Cr
50 mg/L Ba, Cd, Ag, Zn, Mn

Single Element Stock Solutions 1000 mg/L

Sb Ag
Be Na
Ca V
Cr Zn
Mg Sn

Calibration Standard #1:

1. **For Al, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Ag, Na, V, Zn:** Into a 1 L volumetric flask, add 500 mL of de-ionized (D.I.) water and 50 mL of concentrated HCl. Pipet 10 mL each of XWE-1, XWE-2, XWE-3a, and XWE-4a. Dilute to volume with D.I. water.

2. **For Sb:** Into a 500 mL volumetric flask, add 250 mL of D.I. water and 25 mL of concentrated HCl. Pipet 1.0 mL of 1000 mg/L Sb stock solution. Dilute to volume with D.I. water.

3. **For Sn:** Into a 500 mL volumetric flask, add 250 mL of D.I. water and 25 mL of concentrated HCl. Pipet 5.0 mL of 1000 mg/L Sn stock solution. Dilute to volume with D.I. water.

Calibration Standard #2:

1. **For Al, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Na, V, and Zn:** First prepare 10X dilutions each of XWE-1, XWE-2, XWE-3a, and XWE-4a. Then, into a 1 L volumetric flask, add 500 mL of D.I. water and 50 mL of concentrated HCl. Pipet 1.0 mL of XWE-1 (10X dilution), 5.0 mL of XWE-2 (10X dilution), 5.0 mL of XWE-3a (10X dilution), and 2.0 mL of XWE-4a (10X dilution). Dilute to volume with D.I. water.

2. **For Sb:** Into a 200 mL volumetric flask, add 100 mL of D.I. water and 10 mL of concentrated HCl. Pipet 50 mL of Sb Calibration Standard #1 and dilute to volume with D.I. water.

3. **For Sn:** Into a 200 mL volumetric flask, add 100 mL of D.I. water and 10 mL of concentrated HCl. Pipet 20 mL of Sn Calibration Standard #1 and dilute to volume with D.I. water.

Calibration Standard #3:

1. **For Cr, Ag, V and Zn:** First prepare intermediates as follows:

   50 mg/L Ag and Zn: Into a 100 mL volumetric flask, add 10 mL of 1:1 HCl. Pipet 5.0 mL each of single element Ag and Zn stock solutions and dilute to volume with D.I. water.

   100 mg/L Cr: Into a 100 mL volumetric flask pipet 10.0 mL of single element Cr stock solution. Add 5 mL of 1:1 HCl and dilute to volume with D.I. water.

   50.0 mg/L V: Into a 100 mL volumetric flask pipet 5.0 mL of single element V stock solution. Add 5 mL of 1:1 HCl and dilute to volume with D.I. water.

   Then, into a 500 mL volumetric flask, add 250 mL D.I. water and 25 mL of concentrated HCl. Pipet 1.0 mL of 100 mg/L Cr intermediate, 0.5 mL of 10 mg/L Ag-Zn mixed intermediate, and 2.5 of 50 mg/L V intermediate. Dilute to volume with D.I. water.

2. **For Sb:** Into a 100 mL volumetric flask, add 50 mL of D.I. water and 10 mL of 1:1 HCl. Pipet 50 mL of Calibration Standard #2 and dilute to volume with D.I. water.

Initial Calibration Verification:

1. **For Al, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Ag, Na, V, and Zn:** Into a 1 L volumetric flask, add 500 mL of D.I. water and 50 mL of concentrated HCl. Pipet 10 mL of XWE-6a, 10 mL of 1000 mg/L Mg stock, 10 mL of 1000 mg/L Ca stock, and 20 mL of 1000 mg/L Na stock solutions. Dilute to volume with D.I. water.

2. **For Sb:** Into a 500 mL volumetric flask, add 250 mL of D.I. water and 25 mL of concentrated HCl. Pipet 0.5 mL of 1000 mg/L Sb stock and dilute to volume with D.I. water.

3. **For Sn:** Into a 1 L volumetric flask, add 500 mL of D.I. water and 50 mL of concentrated HCl. Pipet 2.5 mL of 1000 mg/L Sn stock and dilute to volume with D.I. water.

Continuing Calibration Verification Standard:

1. **For Al, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Ag, Na, V, and Zn:** Into a 1 L volumetric flask, add 500 mL D.I. water and 50 mL of concentrated HCl. Pipet 2.0 mL each of XWE-1, XWE-3a, XWE-4a, and 4.0 mL of XWE-2. Dilute to volume with D.I. water.

2. **For Sb:** Use Sb Initial Calibration Verification Standard.

3. **For Sn:** Into a 200 mL volumetric flask, add 100 mL D.I. water and 10 mL of concentrated HCl. Pipet 1.0 mL of 1000 mg/L Sn stock and dilute to volume with D.I. water.

Effective 4-30-92

ATOMIC ABSORPTION SPECTROMETRY FLAME-DIRECT ASPIRATION

Scope and Application: Metals in solution can be readily analyzed by Atomic Absorption Spectrometry using either flame or furnace techniques. The flame-direct aspiration method can be used for most metals but is generally not as sensitive as the furnace method. Both the air-acetylene and nitrous oxide-acetylene flame techniques are described in this operating procedure as well as the use of emission spectroscopy.

Method: Flame; direct aspiration

Reference: EPA 1984, Section 200

"Analytical Methods for Flame Spectrophotometry", Varian 1979

Spectr AA - 10/20 Operation Manual, Varian

"Statement of Work for Inorganic Analysis", ILM01.0, EPA 1990

Sample Handling: Acidify aqueous samples with concentrated nitric acid to pH<2. All samples must be digested prior to analysis (refer to appropriate digestion procedures). Samples must be analyzed within 6 months from date of collection.

Reagents and Apparatus:

1. Varian Spectr AA-20
2. Stock and standard metal solutions
3. class A volumetric glassware
4. Instra-analyzed nitric acid
5. Deionized (D.I.) water
6. Hollow cathode element lamps
7. Disposable 10 mL beakers
8. Eppendorf 100-1000 uL pipetter
9. Oxford 5 or 10 ml pipetter
10. Acetylene gas
11. Air supply
12. Nitrous oxide gas
13. Air-acetylene burner head or nitrous oxide-acetylene burner head

Setup:

1. Power on instrument. The computer will automatically start with a memory check. When the first screen appears, it is ready to operate.

   Note: Allow the instrument to warm up for one half hour before beginning analysis to allow for thermal equilibrium of electronic and optical components.

2. Power on printer. Check the paper supply.

3. Install the desired element lamp in the lamp turret by depressing the middle white button behind the socket, inserting the lamp, and releasing the button. Ensure that the lamp is secure and that the connections are fitting properly.

   Note: Allow lamp a 10-15 minute warm up period before beginning analysis.

Procedure:

This procedure outlines an analysis as it would be run following the instructions given on sequential computer screens. **Note:** Any time during setup the "Index" key can be used to go to any screen in the software.

1. Soft key selections allow the operator to develop program, modify program, or automatic run. The typical analysis will be run by selecting "Automatic Run."

   Note: After completing required information on the present screen use the soft keys to call up the next screen.

2. **Sequence Selection:** This screen lists the programs on file. Use the "Clear Sequence" soft key to erase the last sequence used, type in the number corresponding to the program desired, and press "Sequence Selection" soft key. This will automatically recall the program.

3. **Sequence Control:** This screen is used for automatic runs and autosampler control. Verify that appropriate values are entered for "first sample" and "last sample", as the flame will shut off automatically when the "last sample" value is reached. Go to next screen by pressing "Report Format" soft key.

4. **Report Format:** Use cursor arrows and numeric keys to enter operator (employee number) and date. The "Home" key is used to change entries of other parameters.

5. **Sample Labels:** Use the cursor arrows and numeric keys to enter all sample labels for the analytical run. It is recommended to include one or two blank labels at the end of the list to allow for the addition of any dilutions required.

Note: Sample labels will only be printed if the automatic run is used.

6. **Optimization:** This screen is used to optimize wavelength and lamp position.

   a. Ensure lamp is in the correct position and is turned on.

   b. Select proper slit width.

   c. Release brake ("off") and set approximate wavelength. Set brake ("on") and fine-tune the wavelength to achieve maximum intensity on Hollow Cathode Lamp (HCL) bar graph. "Rescale" (soft key) as often as necessary to keep graph on scale.

   d. Optimize lamp position using the adjusting screws on back of the lamp socket. Adjust for maximum intensity on the bar graph. "Rescale" as often as necessary.

   e. If background correction is used, adjust maximum intensity on background bar graph by 2 set screws on the background corrector housing. Set attenuator ("In" or "Out") if necessary. "Rescale" if necessary.

   f. Record the photomultiplier voltage in the instrument log book. A constantly increasing voltage over time is evidence of decreasing efficiency of the element lamp. Monitor this voltage to determine when element lamps should be replaced.

   Note: HCL and background lamp intensities should match as closely as possible. The attenuator will decrease the background lamp intensity. A lower lamp current will decrease the intensity of the element lamp

7. **Flame Ignition**

   a. Turn on compressed air to 50 psi (35-65 psi)

   b. Turn on acetylene tank; regulator outlet pressure should be 7-15 psi.

   c. Turn on nitrous oxide tank (if necessary - the proper burner head must be in place for ignition to occur). Regulator outlet pressure should be 50 psi (35-65 psi).

   d. Press "Ignite" key and hold down until flame ignites.

   Note: The burner head should be at thermal equilibrium before beginning an analytical run. Allow a warm-up period of 5 to 10 minutes for an air-acetylene flame, and 10 to 15 minutes for a nitrous oxide-acetylene flame.

8. **Signal Optimization**

   a. Press "Optimize Signal" soft key on optimization screen.

   b. Optimize burner head position using horizontal and diagonal adjustments. While aspirating a high concentration standard, adjust the acetylene flow to achieve maximum signal intensity.

   c. If necessary, adjust the nebulizer impact glass bead by slowly turning the screw directly below the nebulizer. Adjust for maximum signal intensity.

9. **Flame Emission Procedures**

   a. For emission methods, no element lamp or background correction is used. Burner head position and wavelength are optimized while aspirating the highest concentration working standard.

   b. Turn the burner head full right or left (approximately 30° angle).

   c. Select optimization screen.

   d. Adjust wavelength for maximum intensity.

   e. Press "Emission Setup" soft key.

   f. Continue with automatic or non-automatic run procedure.

10. **Automatic Run (no autosampler)**

   Note: Only pre-existing programs can be used.

   a. Press "Start" key to initialize run. Once a run is started, it can be paused by pressing the "Stop" key, but none of the program parameters can be changed during the analytical run.

   b. Press "Instrument Zero" key after program has been recalled to establish a zero instrument baseline.

   c. Aspirate standards or sample and press "Read". The instrument will display the std #/sample # on the top of the screen, along with the absorbance.

   d. The "Previous Sample"/"Next Sample" soft keys can be used to repeat a specific analysis or move ahead in the sample order, "Solution Type" can be used to restandardize starting at "Blank".

e. If more than 66 samples and standards are to be analyzed, add them at the end of the run and press "Previous Sample" key for each sample. Since the sample labels cannot be changed, leave the last few labels blank on the Sample Labels page, and manually write them in when the run is completed.

f. Press "Stop" key to pause or end the analysis.

11. **Non-automatic Run**

Note: A modified or newly developed program can be run in this mode, a well as a pre-existing program.

a. Set up instrument according to previous instruction. Note that the sample labels and report format cannot be printed in this mode.

b. Advance to "Standards" screen by use of soft key on optimization screen or through the "Index".

c. Aspirate standards/samples and press "Read" key as in the automatic run.

d. In this mode there is no limit to the number of samples that can be included in an analytical run. However, sample labels will not be printed automatically and must be manually written.

12. **Instrument Shut Down**

a. Close valve on the acetylene tank, the flame will extinguish when all the acetylene is purged from the line.

b. Recall program #17 or # (Emission programs), so that lamp turret is zero when the instrument is initially turned on.

c. Turn off printer.

d. Turn off instrument.

Effective: 7-2-91

POTASSIUM - VARIAN 20

Method: Flame Emission: Direct Aspiration

Reference: "Analytical Methods for Flame Spectrophotometry, Varian 1979.

"Standard Methods for the Examination of Water and Wastewater", 16th Edition, Method 322B, 1985.

"Statement of Work for Inorganic Analysis", ILM01.0, EPA 1990

Detection Limit: 0.10 mg/L

Optimum Range: 0.10 - 10.0 mg/L

Sample Handling: Acidify with nitric acid to pH <2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Instrument mode: Emission
2. Wavelength: 766.5 nm
3. Slit Width: 1.0
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for calibration: 0.50, 1.00, 2.00, 5.00, 10.0 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. **Standard Potassium Solution (100 mg/L Potassium):** Pipet 10 mL of the 1000 ppm stock potassium solution into a 100 mL volumetric flask, add 0.5 mL HNO_3, and dilute to volume with D.I. water.

2. **Standards:** (Prepare fresh daily.)

Concentration of Standard	Volume of Potassium Standard	Dilute to
0.50 mg/L	0.5 mL of 100 mg/L	100 mL
1.00 mg/L	1 mL of 100 mg/L	100 mL
2.00 mg/L	2 mL of 100 mg/L	100 mL
5.00 mg/L	5 mL of 100 mg/L	100 mL
10.0 mg/L	10 mL of 100 mg/L	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual.

If potassium is to be analyzed in concentration mode, use the 1.00, 5.00, and 10.0 mg/L standards to calibrate the instrument and follow the procedure for analyzing in the concentration mode.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The emission readings should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, etc.).

2. A quality control calibration standard of 1.00 mg/L and a blank are to be analyzed, initially and after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

4. An EPA reference sample will be analyzed with each analysis.

Calculations:

1. Calculate using the instrument concentration mode, or

2. For method of standard additions, use linear regression.

[rff-metcont-280]

Effective: 7-2-91

SODIUM - VARIAN 20

Method: Flame Emission: Direct Aspiration

Reference: "Standard Methods for the Examination of Water and Wastewater", 16th Edition, Method 325B, 1985

"Analytical Methods for Flame Spectrophotometry", Varian, 1979

"Statement of Work for Inorganic Analysis", ILM01.0, EPA 1990

Detection Limit: 1.0 mg/L

Optimum Range: 1.0 - 100 mg/L

Sample Handling: Acidify with nitric acid to pH <2. Drinking waters and filtered groundwater free of particulate matter and organics may be analyzed directly, while wastewaters, leachates, solids, etc. must be digested prior to analysis (refer to appropriate digestion procedures). Analyze within 6 months.

Instrument Conditions:

1. Set signal to emission. (No lamp is required.)
2. Wavelength: 589.0 nm
3. Slit Width: 0.2 Normal
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing, lean, blue
7. Standards to use for curve set-up: 1.0, 5.0, 10.0, 25.0, 50.0, 75.0, 100.0 mg/L.

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. **Standard Sodium Solution (100 mg/L Sodium):** Pipet 10 mL of the 1000 ppm stock sodium solution into a 100 mL volumetric flask, add 1/2 mL HNO_3, and dilute to the mark with D.I. water.

2. **Standards:** (Prepare fresh daily.)

Concentration of Standard	Volume of Sodium Standard	Dilute to
1.0 mg/L	1 mL of 100 mg/L Na	100 mL
5.0 mg/L	5 mL of 100 mg/L Na	100 mL
10.0 mg/L	1 mL of 1000 mg/L Na	100 mL
25.0 mg/L	2.5 mL of 1000 mg/L Na	100 mL
50.0 mg/L	5 mL of 1000 mg/L Na	100 mL
75.0 mg/L	7.5 mL of 1000 mg/L Na	100 mL
100.0 mg/L	10 mL of 1000 mg/L Na	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Flame - Direct Aspiration section of this manual but make the following changes:

1. Turn the burner head counter clockwise as far as it will go (approximately a 45° angle).

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The emission readings should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, etc.).

2. A quality control calibration standard of 25.0 mg/L and a blank are to be analyzed, initially and after every 10 samples. If less than 10 samples are analyzed, a calibration standard and blank are still required. The last samples analyzed in the run are to be the calibration standard and blank. These standards must be within the acceptable ranges or the samples run after the last acceptable check standard are to be reanalyzed.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

4. An EPA reference sample will be analyzed with each analysis.

Calculations:

1. Calculate using instrument concentration mode, or

2. For method of standard additions, use linear regression.

[rff-metcont-276]

Effective Date: 4-28-92

ATOMIC ABSORPTION SPECTROMETRY
Furnace - Direct Injection

Scope and Application: Metals in solution can be readily analyzed by Atomic Absorption Spectrometry using either flame, furnace or hydride techniques. The furnace - direct injection technique allows for lower detection limits. The use of the graphite platform in furnace analyses can improve sensitivity and reduce some matrix interferences.

Method: Furnace; direct injection

Reference: "Methods for Chemical Analysis of Water and Wastes", EPA 1984, Section 200
"Test Methods for Evaluating Solid Waste - Physical/Chemical Methods", 3rd Edition, EPA November 1986
"Analytical Methods for Zeeman Graphite Tube Atomizers" - Varian 1986
"Spectra AA - 300/400 Zeeman Operation Manual" - Varian March 1988

Sample Handling: Acidify aqueous samples with concentrated nitric acid to ph< 2. All samples must be digested prior to analysis (refer to the appropriate digestion procedures). Samples must be analyzed within 6 months of the sample collection date.

Reagents and Apparatus:

1. Zeeman Atomic Absorption Spectrometer - 400
2. Zeeman Graphite tube Atomizer
3. IBM Personal System/2 Model 30 Computer
4. EPSON EX-800 Printer, Citizen HSP-500 printer, or similar adaptable printer.
5. Required metal lamp and power source
6. Stock and standard solutions for required metal
7. Class A volumetric glassware
8. Instr-analyzed nitric acid
9. Deionized (D.I.) water
10. Argon gas - prepurified grade
11. Graphite partition tubes
12. Graphite plateau tubes and platforms
13. Disposable 2 mL sample cups
14. Eppendorf 100-1000 microliter pipetor
15. Disposable 10 ml beakers

Procedure:

Power Up Procedure

1. Turn on argon gas and cooling water.

2. **Always turn the system on in the following order:** spectrometer, furnace, printer, and computer. This initializes the communication relays correctly so that all components of the system can "talk" to each other.

3. After the DOS prompt has been displayed, type "Zeeman" and press Enter. After a brief pause, an introductory message will then be displayed followed by the PROGRAM MODES page. Follow the on-screen instructions to select the appropriate mode.

Automatic Run Using the Sampler:

Notes:

a. Only programs which have been stored can be used for an automatic run.

b. For all programs, the method of sample introduction (**instrument parameters** page) must be specified as **sampler automixing** (for automatic mixing of calibration standards from a single, high concentration standard) or **sampler premixed** (for a full set of calibration standards that are prepared by the operator prior to analysis).

c. Options on the **report format** page allow raw data to be printed either as it is collected during an analytical run (used for most analyses), or after the analysis is completed (used for sequential runs of multiple elements).

d. If an automatic run is stopped and then restarted, the sampler will automatically perform a tube clean and analyze a blank. It will then continue on according to the instructions set in the **sequence control** page.

e. F9 through F12 are hard keys with their function on the supplied overlay. F1 through F6 are soft keys; their functions will change from one page to the next. The function for each soft key is displayed at the bottom of the screen and only those displayed are active for that page.

f. Any page described below can be recalled by returning to the **index** and entering the appropriate page number.

1. Perform daily maintenance. Check the condition of the graphite tube and replace as necessary.

2. From the **program modes** page, press **automatic run.** The system will automatically display the **sequence selection** page.

3. On the **sequence selection** page, press F1 to clear the sequence of previous element(s) and enter the number of the program to be run. If more than one program is to be run, press **enter** after each element program number. Press F6 to recall program. The **sequence control** page will automatically be displayed.

4. Follow on-screen instructions to enter the number of initial tube burns for cleaning (1 or 2 for previously used furnace tubes, 3 or 4 burns for new tubes), the starting position for the run (usually position #1), and the last position for the run. Note that when the analysis at the last position is completed, the automatic run is terminated and the element lamp is shut off automatically. Setting the final position to leave several empty cups at the end of the analytical run allows necessary repeats or dilutions to be added to the end of the current run, saving lamp warm-up and calibration time.

5. Return to the **index** and select page 6 (**optimization**)

   a. Open the lamp turret cover and ensure that the required lamp is in the operating position.

   b. Observe the signal bar labelled **align hc lamp** displayed on the video screen. Turn the horizontal lamp base adjusting screw (the top one of the two) fully clockwise. Now turn this screw slowly counter-clockwise until the first peak is detected (the length of the signal bar will increase). Continue adjusting this screw until the length of the signal bar is the maximum obtainable (if the signal bar is fully extended, press the rescale soft key, F1, to bring the signal bar back on scale and again adjust the screw to obtain maximum signal. Note particularly that turning the horizontal adjusting screw further counter-clockwise may produce a second peak. **Do not** align the lamp on this second peak - **always** align the lamp on the first peak. Carefully adjust the vertical adjusting screw (the bottom one of the two) so that the length of the signal bar is the maximum obtainable (if necessary, press F1 to rescale the signal bar).

c. Record the photomultiplier voltage in the instrument log book. A constantly increasing voltage over time is evidence of decreasing efficiency of the element lamp. Monitor this voltage to determine when element lamps should be replaced.

d. When switching from partition to platform tubes (or vice-versa), check the position of the graphite tube automizer:

Hold a piece of white card between the right furnace window and the sample compartment window. Use the furnace vertical adjust and position the furnace unit until light from the hollow cathode lamp is obviously passing through the graphite tube onto the card.

Remove the card. Observe the signal bar labelled **align hc lamp** displayed on the video screen. Use the furnace vertical adjust and carefully adjust the position of the furnace unit until the length of the signal bar is the maximum obtainable.

5. Use the soft key indicated, or return to **index** to select **standards page**. This page tells which standards are to be used for calibration.

6. Use the soft key indicated, or return to **index** to select **sampler page.** This page lists the volume of standards, blanks, samples and modifier that are to be used for analysis.

7. At the **sampler** page, press F2 to align the sampler arm. Place a finger on the arm as it starts to descend into the furnace and gently lower the arm by hand. Carefully adjust the sampler position using the two adjustment knobs on the base of the autosampler so that the capillary is exactly in the center of the sample injection hole. With the capillary down in the furnace, and using the mirror, turn the height adjusting screw so the capillary is about 1 mm above the bottom of the tube or platform.

8. Return to **index** and select **report format** page. Enter operator initials, analysis date, and batch number. Review the defaults set for the remaining parameters. Follow the on-screen instructions for using the **home** key to make any needed changes.

9. If sample labels are to be printed with the raw data, press F6 and enter appropriate labels. Note that the **Tab** key will jump the cursor to the next field; the ↑ and ↓ keys to move the cursor up and down the columns.

10. Press F10 to zero the instrument before beginning analysis. Press F11 to start the automatic run.

11. To change basic operating conditions (these are default conditions recalled automatically with the analytical program), press F12 to pause run, return to the **index** and select page 4, **instrument parameters**. Parameters may be changed using the **home** key or soft keys as indicated. Press F11 to resume the analytical run.

Furnace Maintenance:

The following maintenance is to be done each day the furnace is operated:

1. Clean the furnace windows.

    a. Twist out furnace windows from furnace unit.
    b. Wipe windows with a Q-tip moistened with alcohol.
    c. Rinse windows with D.I. water and dry with a Kim-Wipe
    d. Re-insert windows in furnace.

2. Check machine windows and clean if needed.

3. Wipe inside of furnace with a Q-tip moistened with alcohol.

4. Fill the autosampler rinse bottle with D.I. water.

5. Open the syringe compartment door on the autosampler and pull the syringe assembly carefully out of its mounting. Remove the plunger from the syringe, and on the **sampler** page, press F3 to rinse the syringe and bleed any air bubbles from the syringe. Press F3 and rinse again, while water is dripping from syringe insert the plunger into the syringe. Wipe the syringe dry and carefully re-insert in its mounting.

6. **Inserting graphite tube**

    a. Swing toggle lever on top of furnace fully clockwise to open furnace.

    b. Place graphite tube in the graphite shroud in the center block. Align sample introduction port of the graphite tube with the opening in the furnace block.

c. Swing the toggle lever fully counter-clockwise and the righthand electrode assembly will automatically close on the center block.

d. Before using a new graphite tube for analyses, use the tube clean utility (**signal graphics** page) 3-4 times to remove any contamination. This can be done automatically by entering 3 or 4 tube cleans in the appropriate field on the **sequence control** (page 11) before starting an analytical run.

Effective Date: 5-7-92

ANTIMONY - VARIAN 400

Method: AA - Furnace; Direct Injection

Reference: "Methods for Chemical Analysis of Water and Wastes", EPA 1984, Method 204.2

"Test Methods for Evaluating Solid Waste - Physical/Chemical Methods", 3rd Edition, EPA November 1986, Method 7041

"Analytical Methods for Zeeman Graphite Tube Atomizers", Varian, 1986

"Statement of Work for Inorganic Analysis", ILM01.0, EPA 1990

Detection Limit: 0.005 mg/L

Optimum Range: 0.005 - 0.100 mg/L

Sample Handling: Acidify aqueous samples with nitric acid to pH <2. Analyze within 6 months. All samples must be digested prior to analysis.

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Area
Lamp Current (mA):	14
Slit Width (nm):	0.2
Slit Height:	Normal
Wavelength (nm):	217.6
Sample Introduction:	Sampler Premixed
Time Constant:	0.05
Measurement Time (sec):	2.0
Replicates:	2
Background Correction:	On
Maximum Absorbance:	1.40

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. The use of halide acids should be avoided.

5. Nickel nitrate is added as a matrix modifier to control interferences.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

Use the 25.0, 50.0, and 100.0 ug/L standards for instrument calibration.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. Immediately after the calibration of the instrument, an initial calibration verification (ICV) standard of 25.0 ug/L and calibration blank (ICB) are to be analyzed. Thereafter, a continuing calibration verification (CCV) standard of 50.0 ug/L and a calibration blank (CCB) must be analyzed after every 10 analytical samples or after every 20 burns, whichever is more frequent. If less than 10 samples are analyzed, a CCV and CCB are still required. The last samples analyzed in the run are to be a CCV and CCB. These standards must be within 90-110% of the true value, or the analysis must be stopped, the problem corrected, the instrument recalibrated, and all samples following the last acceptable CCV are to be reanalyzed starting with a CCV and CCB.

3. Analyze a standard at, or less than, the contract required detection limit after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required. (See the Furnace Decision Tree for more detail.)

6. An EPA reference standard will be analyzed with each analysis.

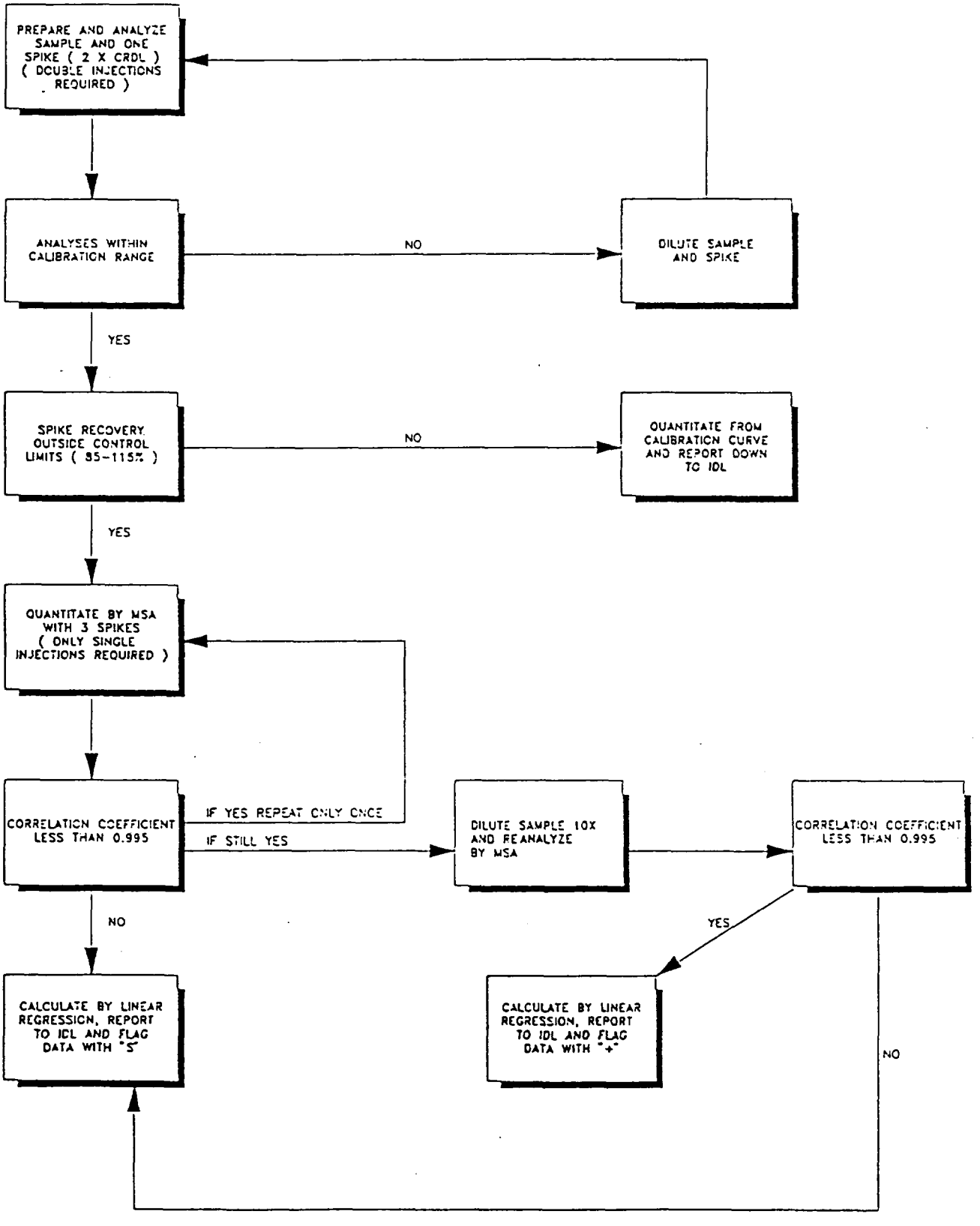
Calculations:

1. Calculate using the instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

WARZYN

FURNACE CLP DECISION TREE



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Effective Date: 4-28 92

ARSENIC - VARIAN 400

Method: AA - Furnace; Direct Injection

Reference: "Methods for Chemical Analysis of Water and Wastes", EPA 1984, Method 206.2

"Test Methods for Evaluating Solid Waste - Physical/Chemical Methods", 3rd Edition, EPA November 1986, Method 7060

"Analytical Methods for Zeeman Graphite Tube Atomizers"-Varian, 1986

"Statement of Work for Inorganic Analysis", ILM01.0, EPA 1990

Detection Limit: 0.002 mg/L

Optimum Range: 0.002 - 0.050 mg/L

Sample Handling: Acidify aqueous samples with nitric acid to pH <2. Analyze within 6 months. All samples must be digested prior to analysis.

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Area
Lamp Current (mA):	10
Slit Width (nm):	1.0
Slit Height:	Normal
Wavelength (nm):	193.7
Sample Introduction:	Sampler Premixed
Time Constant:	0.05
Measurement Time (sec):	1.0
Replicates:	2
Background Correction:	On
Maximum Absorbance:	0.95

FURNACE PARAMETERS

Hot inject samples at 125° C

Step	Temp (°C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	220	1.0	3.0	NORMAL	NO
2	240	35.0	3.0	NORMAL	NO
3	240	5.0	3.0	NORMAL	NO
4	1400	5.0	3.0	NORMAL	NO
5	1400	10.0	3.0	NORMAL	NO
6	1400	1.0	0.0	NORMAL	NO
7	2600	0.8	0.0	NORMAL	YES
8	2600	2.0	0.0	NORMAL	YES
9	2600	1.0	3.0	NORMAL	NO

Sample Volume: 20 uL

Matrix modifier volume: 5 uL (0.25% nickel nitrate).

Calibration standards: 10.00, 20.00, 50.00 ug/L.

Hot Inject: Yes, Temp = 125° C.

Graphite Tube Type: Pyrolytic coated plateau tube

Reagent Preparation:

1. **Standard Arsenic Solution (1000 ug/L Arsenic):** Pipet 1.00 mL of the 1000 ppm stock arsenic solution into a 1000 mL volumetric flask, add 0.5 mL HNO_3 and dilute to the mark with deionized water. Prepare fresh monthly.

2. **Calibration standards:** Digest according to the appropriate digestion procedure. Prepare fresh monthly.

Concentration of Standard	Volume of Arsenic Standard	Dilute to
0 ug/L	0 mL of 1000 ug/L As	100 mL
10 ug/L	1 mL of 1000 ug/L As	100 mL
20 ug/L	2 mL of 1000 ug/L As	100 mL
50 ug/L	5 mL of 1000 ug/L As	100 mL

3. Nickel Nitrate (0.25%): In a 100 mL volumetric flask dissolve 1.25 g of $Ni(NO_3)_2 \cdot 6H_2O$ in D.I. water and dilute to 100 mL. Prepare fresh every 6 months.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. Nickel nitrate is added as a matrix modifier to minimize volatilization losses during the drying and charring steps.

4. The use of background correction is required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

Use the 10.0, 20.0, and 50.0 ug/L standards for instrument calibration.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. Immediately after the calibration of the instrument, an initial calibration verification (ICV) standard of 10.0 ug/L and calibration blank (ICB) are to be analyzed. Thereafter, a continuing calibration verification (CCV) standard of 20.0 ug/L and a calibration blank (CCB) must be analyzed after every 10 analytical samples or after every 20 burns, whichever is more frequent. If less than 10 samples are analyzed, a CCV and CCB are still required. The last samples analyzed in the run are to be a CCV and CCB. These standards must be within 90-110% of the true value, or the analysis must be stopped, the problem corrected, the instrument recalibrated, and all samples following the last acceptable CCV are to be reanalyzed starting with a CCV and CCB.

3. Analyze a standard at, or less than, the contract required detection limit of 10 ug/L after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required. (See the Furnace Decision Tree for more detail.)

6. An EPA reference sample will be analyzed with each analysis.

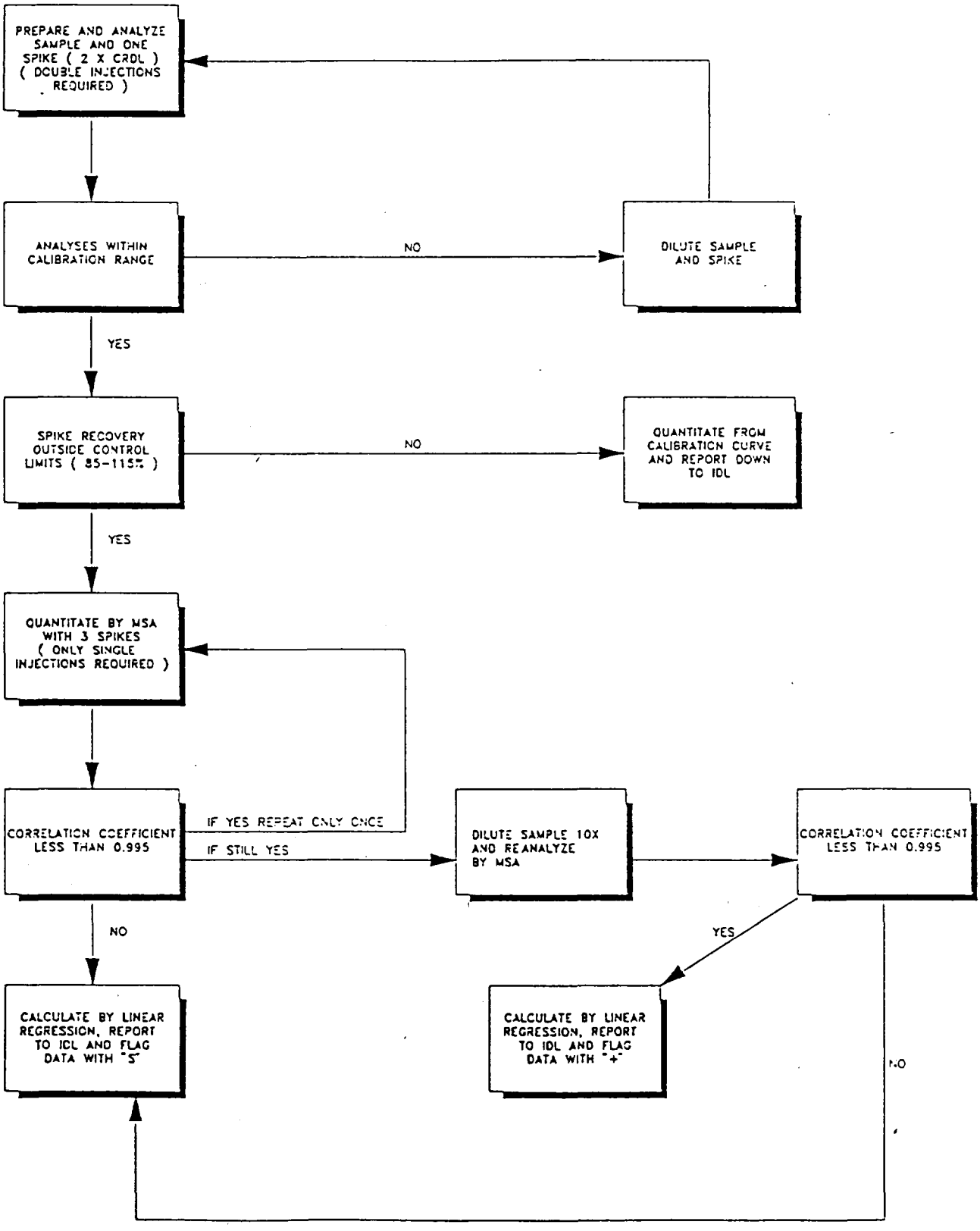
Calculations:

1. Calculate using the instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

WARZYN

FURNACE CLP DECISION TREE



Effective Date: 4-28-92

CADMIUM - VARIAN 400

Method: AA - Furnace; Direct Injection

Reference: "Methods for Chemical Analysis of Water and Wastes", EPA 1984, Method 213.2

"Analytical Methods for Zeeman Graphite Tube Atomizers", Varian, 1986

"Statement of Work for Inorganic Analysis", ILM01.0, EPA 1990

Detection Limit: 0.0002 mg/L

Optimum Range: 0.0002 - 0.0030 mg/L

Sample Handling: Acidify aqueous samples with nitric acid to pH <2. Analyze within 6 months. All samples must be digested prior to analysis.

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Area
Lamp Current (mA):	3
Slit Width (nm):	0.5
Slit Height:	Normal
Wavelength (nm):	228.8
Sample Introduction:	Sampler Premixed
Time Constant:	0.05
Measurement Time (sec):	1.0
Replicates:	2
Background Correction:	On
Maximum Absorbance:	0.70

FURNACE PARAMETERS

Hot inject samples at 125R C

Step	Temp (RC)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	230	1.0	3.0	NORMAL	NO
2	260	35.0	3.0	NORMAL	NO
3	260	5.0	3.0	NORMAL	NO
4	700	5.0	3.0	NORMAL	NO
5	700	5.0	3.0	NORMAL	NO
6	700	1.0	0.0	NORMAL	NO
7	2000	0.8	0.0	NORMAL	YES
8	2000	2.0	0.0	NORMAL	YES
9	2000	2.0	3.0	NORMAL	NO

Sample Volume: 12 uL

Matrix Modifier Volume: 4 uL (Monobasic ammonium phosphate)

Calibration standards: 1.00, 2.00, 3.00 ug/L

Hot Inject: Yes, Temp = 125R C.

Graphite Tube Type: Pyrolytic coated plateau tube

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. **Standard Cadmium Solution (1000 ug/L Cadmium):** Pipet 1.00 mL of the 1000 ppm stock cadmium solution into a 1000 mL volumetric flask, add 0.5 mL HNO_3, and dilute to the mark with D.I. water. Prepare fresh daily.

2. **Working Cadmium Solution (100 ug/L Cadmium):** Pipet 10 mL of the 1000 ug/L cadmium into a 100 mL volumetric flask and dilute to the mark with D.I. water. Prepare fresh daily.

3. Standards (Prepare fresh daily.):

Concentration of Standard	Volume of Cadmium Standard	Dilute to
1.00 ug/L	1 mL of 100 ug/L Cd	100 mL
2.00 ug/L	2 mL of 100 ug/L Cd	100 mL
3.00 ug/L	3 mL of 100 ug/L Cd	100 mL

4. **Monobasic Ammonium Phosphate Solution (1% w/v):** Add 1.0 g of ammonium phosphate (monobasic) to a 100 mL volumetric flask. Dissolve in D.I. water and dilute to volume.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. The cadmium flame or ICP procedure is recommended where concentrations are greater than 0.10 mg/L.

5. Ammonium phosphate is added as a matrix modifier to improve peak shape and allow higher ashing temperatures.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

Use of peak area is required.

Use the 1.00, 2.00, and 3.00 ug/L standards for instrument calibration.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. Immediately after the calibration of the instrument, an initial calibration verification (ICV) standard of 1.00 ug/L and calibration blank (ICB) are to be analyzed. Thereafter, a continuing calibration verification (CCV) standard of 2.00 ug/L and a calibration blank (CCB) must be analyzed after every 10 analytical samples or after every 20 burns, whichever is more frequent. If less than 10 samples are analyzed, a CCV and CCB are still required. The last samples analyzed in the run are to be a CCV and CCB. These standards must be within 90-110% of the true value, or the analysis must be stopped, the problem corrected, the instrument recalibrated, and all samples following the last acceptable CCV are to be reanalyzed starting with a CCV and CCB.

3. Analyze a standard at, or less than, the contract required detection limit after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required. (See Furnace Decision Tree for more detail.)

6. An EPA reference sample will be analyzed with each analysis.

Calculations:

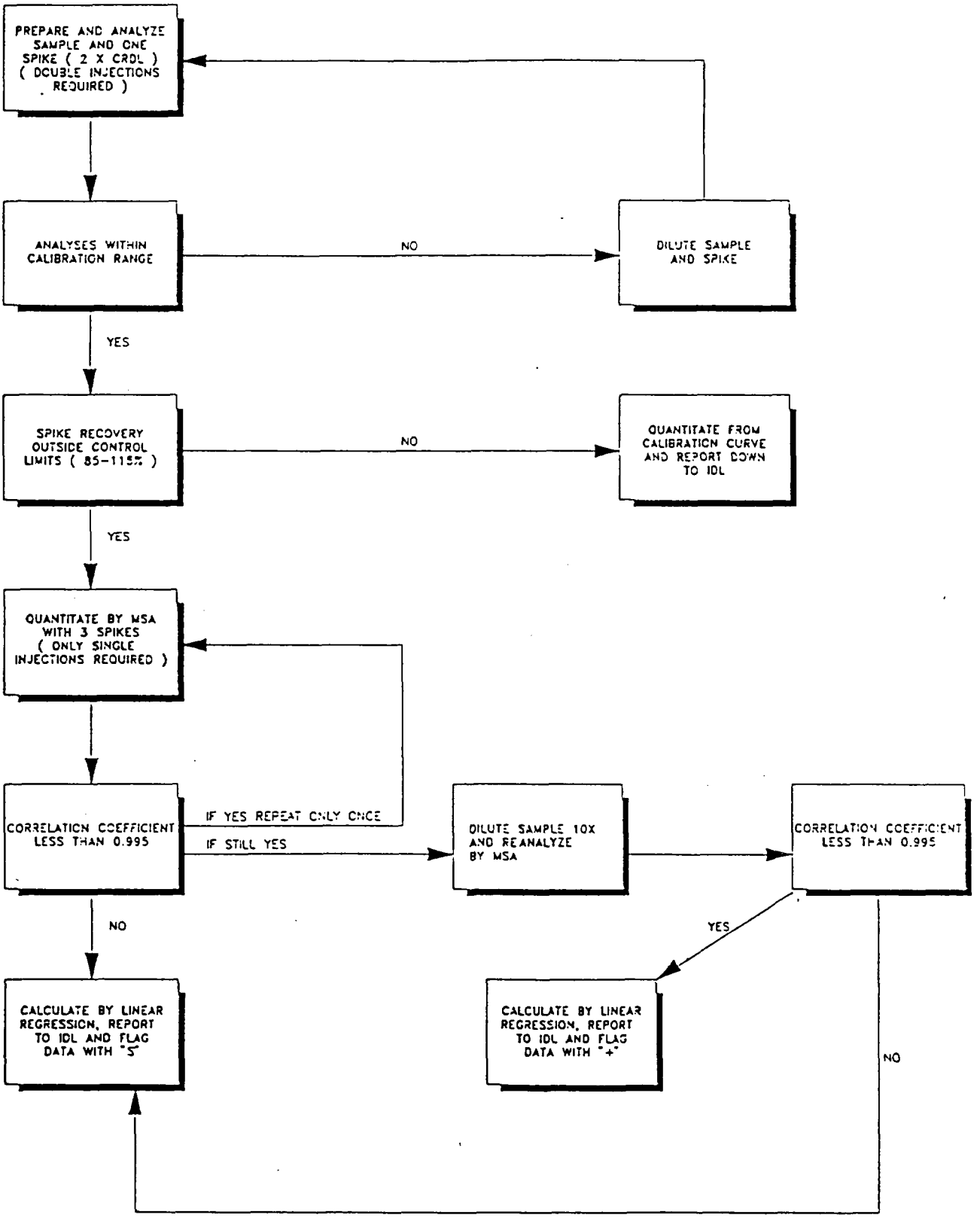
1. Calculate using instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

[rff-metcont-292]

WARZYN

FURNACE CLP DECISION TREE



Effective Date: 4-30-92

CHROMIUM - VARIAN 400

Method: AA - Furnace; Direct Injection

Reference: "Methods for Chemical Analysis of Water and Wastes", EPA 1984, Method 218.2.

"Analytical Methods for Zeeman Graphite Tube Atomizers", Varian, 1986

"Statement of Work for Inorganic Analysis", ILM01.0, EPA 1990

Detection Limit: 0.0002 mg/L

Optimum Range: 0.0002 - 0.010 mg/L

Sample Handling: Acidify aqueous samples with nitric acid to pH <2. Analyze within 6 months. All samples must be digested prior to analysis.

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Area
Lamp Current (mA):	7
Slit Width (nm):	0.2
Slit Height:	Reduced
Wavelength (nm):	357.9
Sample Introduction:	Sampler Premixed
Time Constant:	0.05
Measurement Time (sec):	1.0
Replicates:	2
Background Correction:	On
Maximum Absorbance:	2.00

FURNACE PARAMETERS

Hot inject samples at 95° C

Step	Temp (°C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	105	5.0	3.0	NORMAL	NO
2	120	12.0	3.0	NORMAL	NO
3	150	3.0	3.0	NORMAL	NO
4	1000	10.0	3.0	NORMAL	NO
5	1000	5.0	3.0	NORMAL	NO
6	1000	2.0	0.0	NORMAL	NO
7	2600	1.2	0.0	NORMAL	YES
8	2600	2.0	0.0	NORMAL	YES
9	2600	2.0	3.0	NORMAL	NO

Sample Volume: 20 uL

Matrix Modifier Volume: 5 uL of mixed calcium nitrate/H_2O_2 solution

Calibration standards: 2.00, 5.00, 10.0 ug/L.

Hot Inject: Yes, Temp = 95° C.

Graphite Tube Type: Pyrolytic coated partition tube

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. **Standard Chromium Solution (1000 ug/L Chromium):** Pipet 1.00 mL of the 1000 ppm stock Chromium solution into a 1000 mL volumetric flask, add 0.5 mL HNO_3, and dilute to volume with D.I. water. Prepare fresh daily.

2. **Working Chromium Standard (100 ug/L Chromium):** Pipet 10 mL of the 1000 ug/L chromium into a 100 mL volumetric flask and dilute to volume with D.I. water. Prepare fresh daily.

3. **Standards:** (Prepare fresh daily.)

Concentration of Standard	Volume of Chromium Standard	Dilute to
2.00 ug/L	2.0 mL of 100 ug/L Cr	100 mL
5.00 ug/L	5.0 mL of 100 ug/L Cr	100 mL
10.0 ug/L	10.0 mL of 100 ug/L Cr	100 mL

4. **Calcium Nitrate/Peroxide Solution:** Dissolve 0.59 grams of $Ca(NO_3)_2 \cdot 4H_2O$ in approximately 75 mL of D.I. water in a 100 mL volumetric flask. Add 5.0 mL 30% H_2O_2 and dilute to volume with D.I. water (solution contains 1000 mg/L Ca).

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - direct Injection section of this manual.

Use the 2.00, 5.00 and 10.0 ug/L standards for instrument calibration.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. Immediately after the calibration of the instrument, an initial calibration verification (ICV) standard of 5.00 ug/L and calibration blank (ICB) are to be analyzed. Thereafter, a continuing calibration verification (CCV) standard of 5.00 ug/L and a calibration blank (CCB) must be analyzed after every 10 analytical samples or after every 20 burns, whichever is more frequent. If less than 10 samples are analyzed, a CCV and CCB are still required. The last samples analyzed in the run are to be a CCV and CCB. These standards must be within 90-110% of the true value, or the analysis must be stopped, the problem corrected, the instrument recalibrated, and all samples following the last acceptable CCV are to be reanalyzed starting with a CCV and CCB.

3. Analyze a standard at, or less than, the contract required detection limit after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required. (See Furnace Decision Tree for more detail.)

6. An EPA reference sample will be analyzed with each analysis.

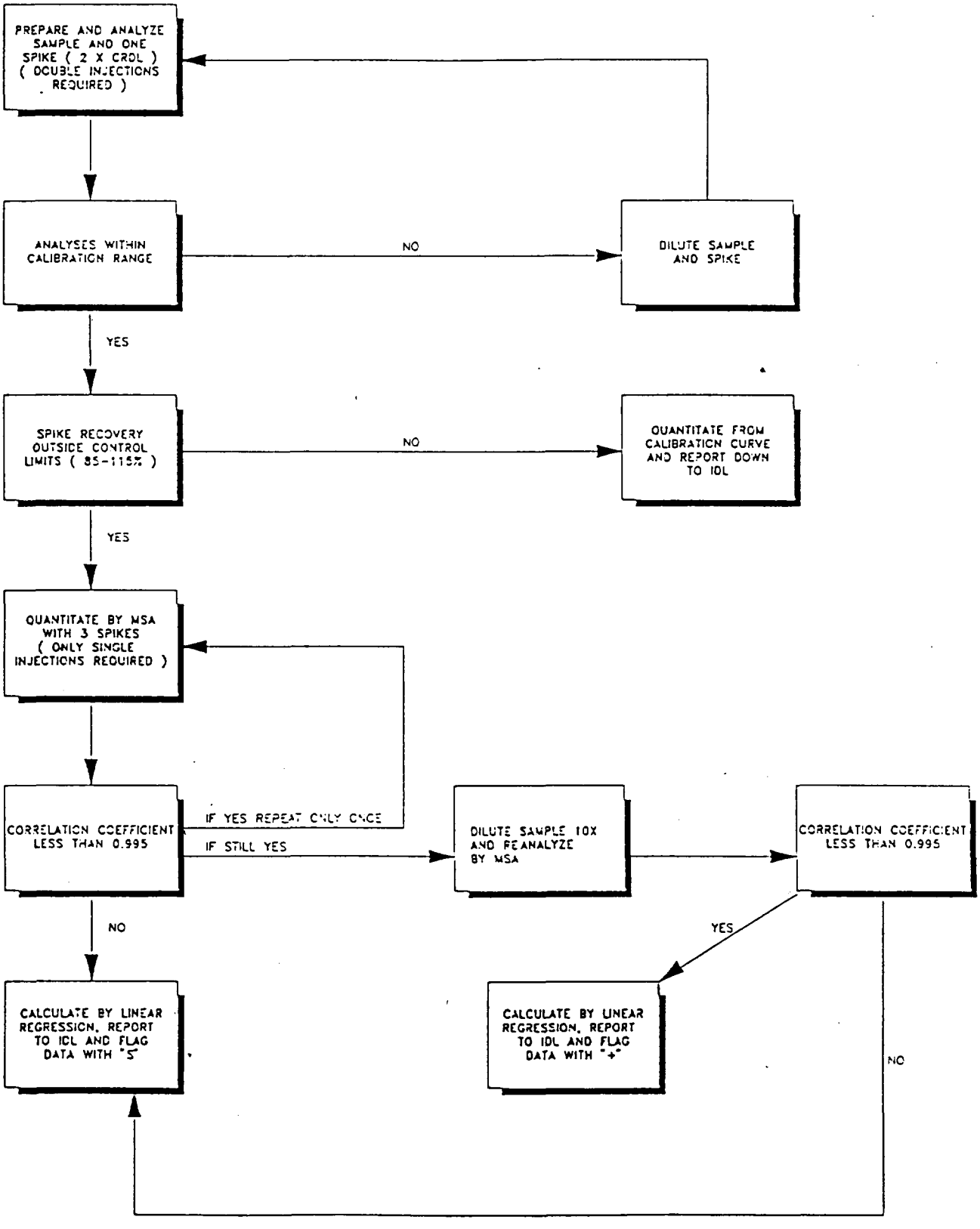
Calculations:

1. Calculate using instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

WARZYN

FURNACE CLP DECISION TREE



Effective Date: 4-30-92

LEAD - VARIAN 400

Method: AA - Furnace; Direct Injection

Reference: "Methods for Chemical Analysis of Water and Wastes", EPA 1984, Method 239.2

"Analytical Methods for Zeeman Graphite Tube Atomizers", Varian, 1986.

"Statement of Work for Inorganic Analysis", ILM01.0, EPA 1990

Detection Limit: 0.003 mg/L

Optimum Range: 0.003 - 0.050 mg/L

Sample Handling: Acidify aqueous samples with nitric acid to pH <2. Analyze within 6 months. All samples must be digested prior to analysis.

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Area
Lamp Current (mA):	4
Slit Width:	0.5
Slit Height:	Normal
Wavelength	283.3
Sample Introduction:	Sampler Premixed
Time Constant:	0.05
Measurement Time (sec):	1.0
Replicates:	2
Background:	On
Maximum Absorbance:	1.40

FURNACE PARAMETERS

Hot inject samples at 125RC

Step	Temp (RC)	Time (sec)	Gas Flow (L/Min)	Gas Type	Read Command
1	220	1.0	3.0	NORMAL	NO
2	240	35.0	3.0	NORMAL	NO
3	240	5.0	3.0	NORMAL	NO
4	650	5.0	3.0	NORMAL	NO
5	650	15.0	3.0	NORMAL	NO
6	650	1.0	0.0	NORMAL	NO
7	2200	0.9	0.0	NORMAL	YES
8	2200	2.0	0.0	NORMAL	YES
9	2500	2.0	3.0	NORMAL	NO

Sample Volume: 20 uL

Matrix modifier volume: 5 uL 0.5% w/v Ammonium Phosphate Monobasic or 5 ul of lanthanum nitrate modifier.

Calibration standards: 3.0, 10.0, 20.0, 50.0 ug/L

Hot Inject: Yes, Temp = 125RC.

Graphite Tube Type: Pyrolytic Coated Plateau Tube

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. **Standard lead solution (10.0 mg/L Lead):** Pipet 1.0 mL of the 1000 ppm stock lead solution into a 100 mL volumetric flask, add 0.5 mL HNO_3 and dilute to volume with deionized water. Prepare fresh daily.

2. **Standard lead solution (100ug/L Lead):** Pipet 1.0 mL of the 10.0 mg/L lead standard into a 100 mL volumetric flask, add 0.5 mL HNO_3 and dilute to volume with deionized water. Prepare fresh daily.

3. **Standards:** (Prepare fresh daily.)

Concentration of Standard	Volume of Lead Standard	Dilute to
3.0 ug/L	3 mL of 100 ug/L Pb	100 mL
10.0 ug/L	10 mL of 100 ug/L Pb	100 mL
20.0 ug/L	20 mL of 100 ug/L Pb	100 mL
50.0 ug/L	50 mL of 100 ug/L Pb	100 mL

4. **Ammonium phosphate matrix modifier (0.5% w/v):** Dissolve 0.5g ammonium phosphate monobasic in 100mL D.I. water.

5. **Lanthanum nitrate matrix modifier:** Dissolve 5.864g of La_2O_3 in 10 ml concentrated nitric acid and dilute to 1 L with D.I. water.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. Ammonium phosphate is added as a matrix modifier to improve peak shape and allow higher ashing temperatures. Ammonium phosphate is the preferred matrix modifier for groundwater, residential wells, and any other samples where chloride or sulfate concentrations are expected to be less than 100 mg/L. Due to its more corrosive nature, lanthanum nitrate should be used as matrix modifier only if chloride and/or sulfate concentrations are expected to exceed 100 mg/L.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

Use the 3.0, 10.0, 20.0 and 50.0 ug/L standards for instrument calibration.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. Immediately after the calibration of the instrument, an initial calibration verification (ICV) standard of 20.0 ug/L and calibration blank (ICB) are to be analyzed. Thereafter, a continuing calibration verification (CCV) standard of 20.0 ug/L and a calibration blank (CCB) must be analyzed after every 10 analytical samples or after every 20 burns, whichever is more frequent. If less than 10 samples are analyzed, a CCV and CCB are still required. The last samples analyzed in the run are to be a CCV and CCB. These standards must be within 90-110% of the true value, or the analysis must be stopped, the problem corrected, the instrument recalibrated, and all samples following the last acceptable CCV are to be reanalyzed starting with a CCV and CCB.

3. Analyze a standard at, or less than, the contract required detection limit after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required. (See Furnace Decision Tree for more detail.)

6. An EPA reference sample will be analyzed with each analysis.

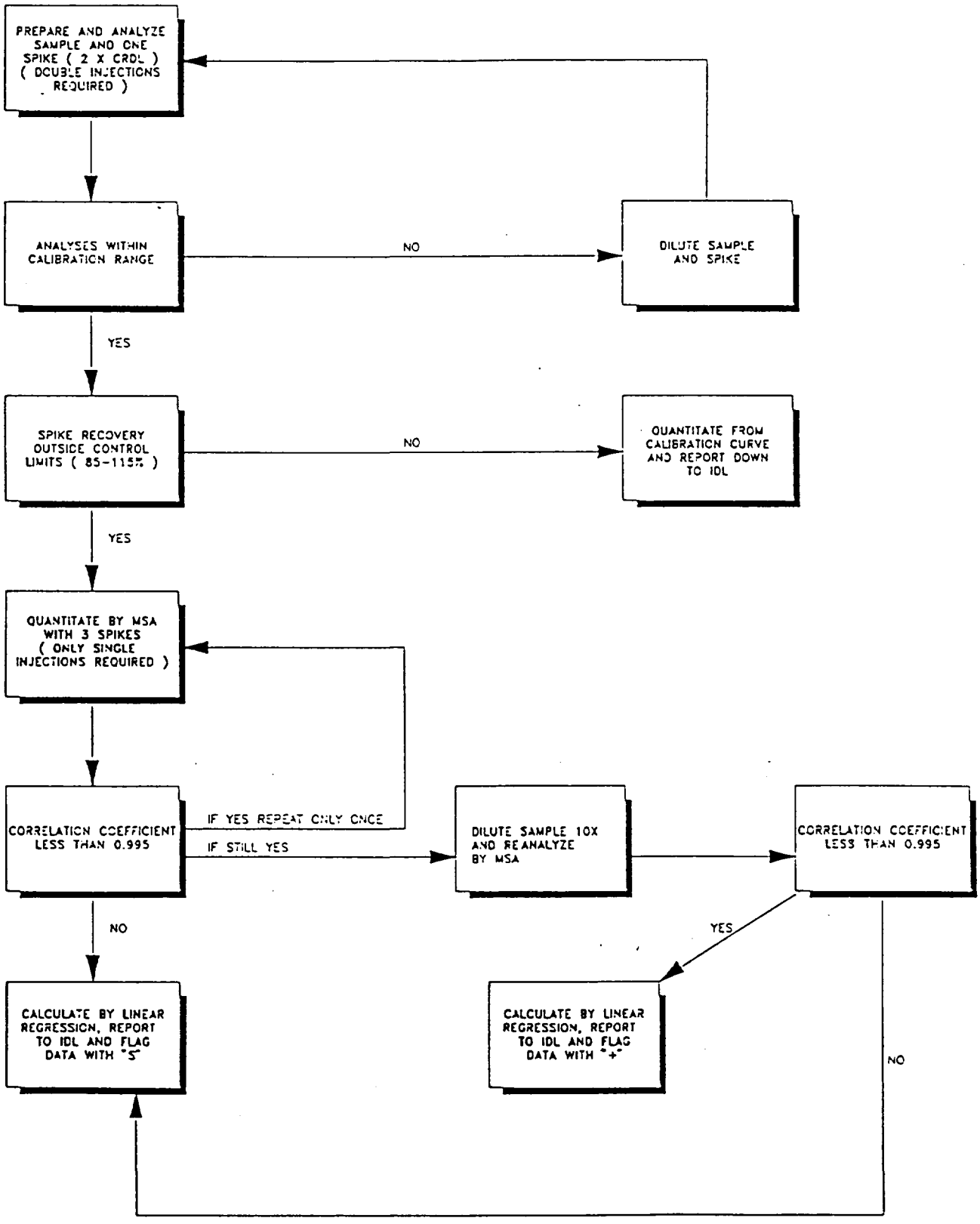
Calculations:

1. Calculate using the instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

WARZYN

FURNACE CLP DECISION TREE



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Effective Date: 4-28-94

SELENIUM - VARIAN 400

Method: AA - Furnace; Direct Injection

Reference: "Methods for Chemical Analysis of Water and Wastes", EPA 1984, Method 270.2

"Analytical Methods for Zeeman Graphite Tube Atomizer"-Varian, 1986

"Statement of Work for Inorganic Analysis", ILM01.0, EPA 1990

Detection Limit: 0.002 mg/L

Optimum Range: 0.002 - 0.050 mg/L

Sample Handling: Acidify aqueous samples with nitric acid to pH <2. Analyze within 6 months. All samples must be digested prior to analysis.

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Height
Lamp Current (mA):	8
Slit Width (nm):	1.0
Slit Height:	Normal
Wavelength (nm):	196.0
Sample Introduction:	Sampler Premixed
Time Constant:	0.05
Measurement Time (sec):	1.0
Replicates:	2
Background Correction:	On
Maximum Absorbance:	1.20

FURNACE PARAMETERS

Hot inject samples at 125°C

Step	Temp (°C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	220	1.0	3.0	NORMAL	NO
2	240	35.0	3.0	NORMAL	NO
3	240	5.0	3.0	NORMAL	NO
4	1400	5.0	3.0	NORMAL	NO
5	1400	10.0	3.0	NORMAL	NO
6	1400	1.0	0.0	NORMAL	NO
7	2600	0.8	0.0	NORMAL	YES
8	2600	2.0	0.0	NORMAL	YES
9	2600	1.0	3.0	NORMAL	NO

Sample Volume: 20 uL

Matrix Modifier Volume: 5 uL (0.25% nickel nitrate)

Standards to use for curve set-up: 5.0, 10.0, 20.0, 50.0 ug/L.

Hot Inject: Yes, Temp = 125°C.

Graphite Tube Type: Pyrolytic coated plateau tube

Reagent Preparation:

1. **Standard selenium solution (1000 ug/L Selenium):** Pipet 1.00 mL of the 1000 ppm stock selenium solution into a 1000 mL volumetric flask, add 0.5 mL HNO_3 and dilute to volume with D.I. Prepare fresh monthly.

2. **Calibration standards:** Digest standards according to the appropriate digestion procedure. Prepare fresh monthly.

Concentration of Standard	Volume of Selenium Standard	Dilute to
5.0 ug/L	0.5 mL of 1000 ug/L Se	100 mL
10.0 ug/L	1 mL of 1000 ug/L Se	100 mL
20.0 ug/L	2 mL of 1000 ug/L Se	100 mL
50.0 ug/L	5 mL of 1000 ug/L Se	100 mL

3. **Nickel Nitrate (0.25%):** In a 100 mL volumetric flask dissolve 1.25 g of $Ni(NO_3)_2 \cdot 6H_2O$ in D.I. water and dilute to 100 mL. Prepare fresh every 6 months.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Chloride (> 800 mg/L) and sulfate (> 200 mg/L) interfere with this selenium procedure. Nickel nitrate is added as a matrix modifier to minimize these interferences.

3. Background correction is required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

Use the 5.0, 10.0, 20.0 and 50.0 mg/L standards for instrument calibration.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. Immediately after the calibration of the instrument, an initial calibration verification (ICV) standard of 10.0 ug/L and calibration blank (ICB) are to be analyzed. Thereafter, a continuing calibration verification (CCV) standard of 20.0 ug/L and a calibration blank (CCB) must be analyzed after every 10 analytical samples or after every 20 burns, whichever is more frequent. If less than 10 samples are analyzed, a CCV and CCB are still required. The last samples analyzed in the run are to be a CCV and CCB. These standards must be within 90-110% of the true value, or the analysis must be stopped, the problem corrected, the instrument recalibrated, and all samples following the last acceptable CCV are to be reanalyzed starting with a CCV and CCB.

3. Analyze a standard at, or less than, the contract required detection limit after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   - If the spike recovery is within 85 - 115%, standard additions are not required.

   - If the spike recovery is outside 85 - 115%, standard additions are required. (See Furnace Decision Tree for more detail.)

6. An EPA reference standard will be analyzed with each analysis.

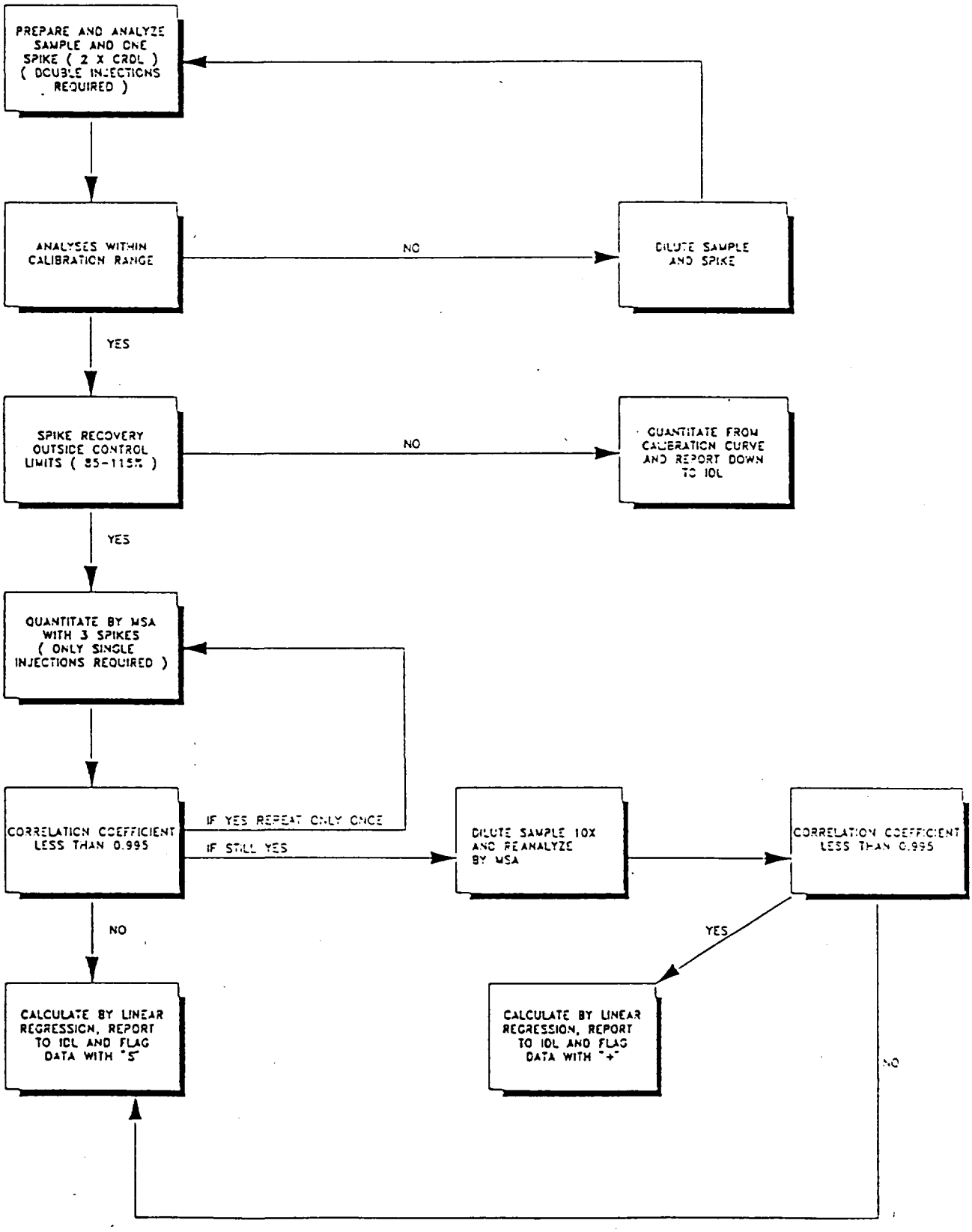
Calculations:

1. Calculate using the instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

WARZYN

FURNACE CLP DECISION TREE



Effective Date: 4-28-92

SILVER - VARIAN 400

Method: AA - Furnace; Direct Injection

Reference: "Methods for Chemical Analysis of Water and Wastes", EPA 1984, Method 272.2

"Analytical Methods for Zeeman Graphite Tube Atomizers", Varian, 1986

"Statement of Work for Inorganic Analysis", ILM01.0, EPA 1990

Detection Limit: 0.0005 mg/L

Optimum Range: 0.0005 - 0.010 mg/L

Sample Handling: Acidify aqueous samples with nitric acid to pH <2. Analyze within 6 months. All samples must be digested prior to analysis.

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Height
Lamp Position:	7
Lamp Current (mA):	4
Slit Width (nm):	0.5
Slit Height:	Normal
Wavelength (nm):	328.1
Sample Introduction:	Sampler Premixed
Time Constant:	0.05
Measurement Time (sec):	1.0
Replicates:	2
Background Correction:	On
Maximum Absorbance:	1.30

FURNACE PARAMETERS

Hot inject samples at 95° C

Step	Temp (°C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	105	5.0	3.0	NORMAL	NO
2	120	12.0	3.0	NORMAL	NO
3	400	5.0	3.0	NORMAL	NO
4	400	1.0	3.0	NORMAL	NO
5	400	2.0	0.0	NORMAL	NO
6	2000	0.9	0.0	NORMAL	YES
7	2000	2.0	0.0	NORMAL	YES
8	2000	2.0	3.0	NORMAL	NO

Sample Volume: 20 uL

Calibration standards: 1.00, 4.00, 10.00 ug/L.

Hot Inject: Yes, Temp = 95° C

Graphite Tube Type: Pyrolytic coated partition tube

Reagent Preparation:

1. **Standard Silver Solution (1000 ug/L Silver):** Pipet 1.00 mL of the 1000 ppm stock silver solution into a 1000 mL volumetric flask, add 5.0 mL HNO_3 and dilute to the mark with D.I. Prepare fresh daily.

2. **Working Silver Standard (100 ug/L Silver):** Pipet 10 mL of the 1000 ug/L silver standard into a 100 mL volumetric flask and dilute to the mark with D.I. Prepare fresh daily.

3. **Standards:** (Prepare fresh daily.)

Concentration of Standard	Volume of Silver Standard	Dilute to
1.00 ug/L	1 mL of 100 ug/L Ag	100 mL
4.00 ug/L	4 mL of 100 ug/L Ag	100 mL
10.0 ug/L	10 mL of 100 ug/L Ag	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. Background correction is required.

4. The use of halide acids should be avoided.

5. Silver standards are light sensitive and tend to plate out on the container walls. Silver standards should be stored in amber glass bottles rather than plastic.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

Use the 1.0, 4.0 and 10.0 ug/L standards for instrument calibration.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. Immediately after the calibration of the instrument, an initial calibration verification (ICV) standard of 1.00 ug/L and calibration blank (ICB) are to be analyzed. Thereafter, a continuing calibration verification (CCV) standard of 4.00 ug/L and a calibration blank (CCB) must be analyzed after every 10 analytical samples or after every 20 burns, whichever is more frequent. If less than 10 samples are analyzed, a CCV and CCB are still required. The last samples analyzed in the run are to be a CCV and CCB. These standards must be within 90-110% of the true value, or the analysis must be stopped, the problem corrected, the instrument recalibrated, and all samples following the last acceptable CCV are to be reanalyzed starting with a CCV and CCB.

3. Analyze a standard at, or less than, the contract required detection limit after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required. (See Furnace Decision Tree for more detail.)

6. An EPA reference standard will be analyzed with each analysis.

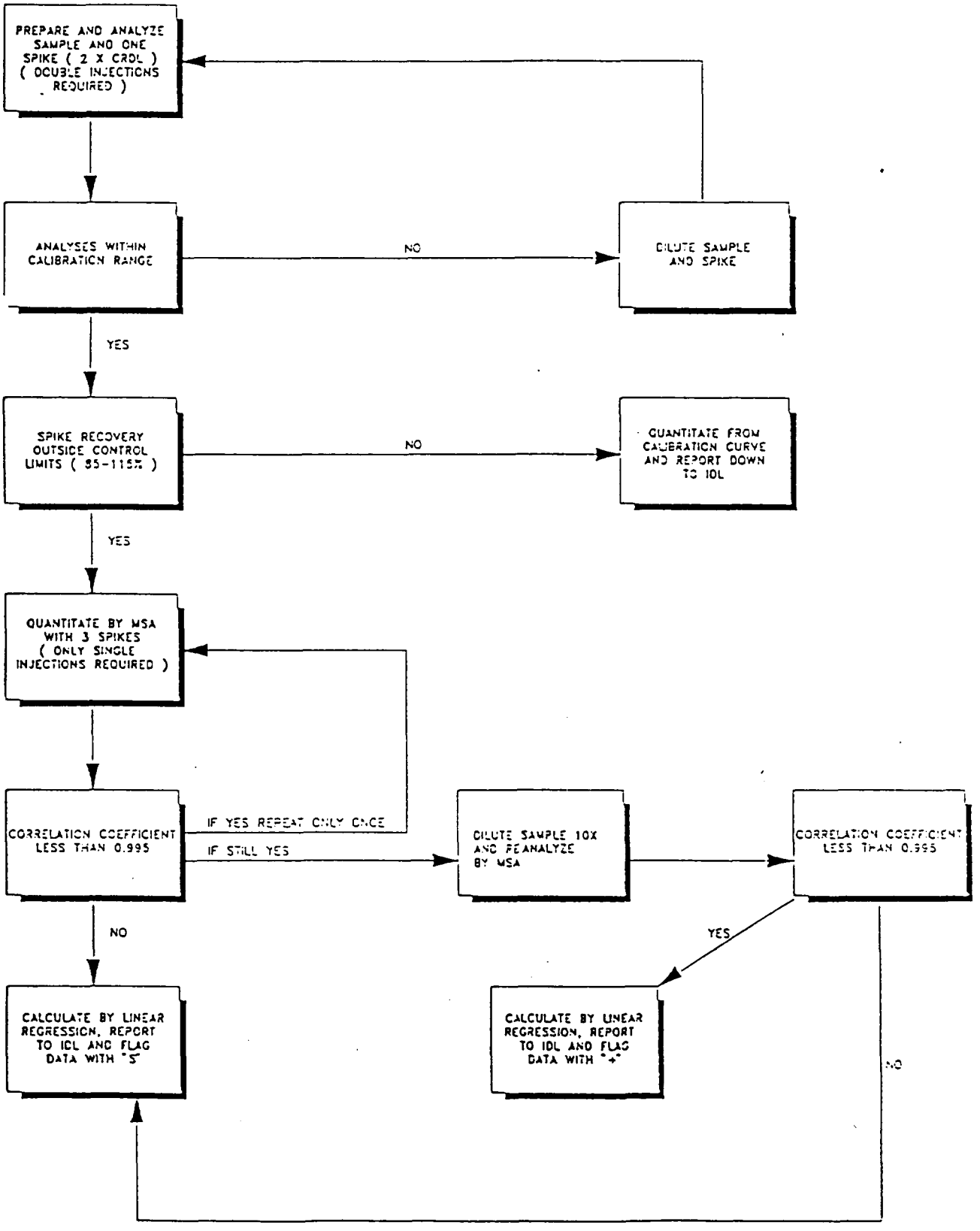
Calculations:

1. Calculate using instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

WARZYN

FURNACE CLP DECISION TREE



Effective Date: 4-28-92

THALLIUM - 400 VARIAN

Method: AA - Furnace; Direct Injection

Reference: "Methods for Chemical Analysis of Water and Wastes", EPA 1984, Method 279.2

"Analytical Methods for Zeeman Graphic Tube Atomizers" - Varian 1986.

"Statement of Work for Inorganic Analysis", ILM01.0, EPA 1990

Detection Limit: 0.003 mg/L

Optimum Range: 0.003 - 0.050 mg/L

Sample Handling: Acidify aqueous samples with nitric acid to pH <2. Analyze within 6 months. All samples must be digested prior to analysis.

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Area
Lamp Current (mA):	10
Slit Width (nm):	0.5
Slit Height:	Normal
Wavelength (nm):	276.8
Sample Introduction:	Sampler Premixed
Time Constant:	0.05
Measurement Time (sec):	1.0
Replicates:	2
Background Correction:	On
Maximum Absorbance:	0.55

FURNACE PARAMETERS

Hot inject samples at 125° C

Step	Temp (°C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	220	3.0	3.0	NORMAL	NO
2	240	35.0	3.0	NORMAL	NO
3	240	5.0	3.0	NORMAL	NO
4	500	5.0	3.0	NORMAL	NO
5	500	10.0	3.0	NORMAL	NO
6	500	1.0	0.0	NORMAL	NO
7	2400	1.0	0.0	NORMAL	YES
8	2400	2.0	0.0	NORMAL	YES
9	2400	1.0	3.0	NORMAL	NO

Sample Volume: 20 uL

Matrix Modifier Volume: 5 uL (1% H_2SO_4)

Calibration standards: 10.00, 25.00, 50.00 ug/L.

Hot Inject: Yes, Temp = 125°C.

Graphite Tube Type: Pyrolytic coated plateau tube

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. **Standard Thallium Solution (1000 ug/L Thallium):** Pipet 1.00 mL of the 1000 ppm stock thallium solution into a 1000 mL volumetric flask, add 0.5 mL HNO_3 and dilute to volume with D.I. water. Prepare fresh daily.

2. **Standards:** (Prepare fresh daily.)

Concentration of Standard	Volume of Thallium Standard	Dilute to
10.0 ug/L	1.0 mL of 1000 ug/L Tl	100 mL
25.0 ug/L	2.5 mL of 1000 ug/L Tl	100 mL
50.0 ug/L	5.0 mL of 1000 ug/L Tl	100 mL

3. **H_2SO_4 1.0% Solution:** Add 1.0 mL of concentrated H_2SO_4 to 90 mL D.I. water. Dilute to 100 mL.

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. 1% H_2SO_4 is added as a matrix modifier.

4. The use of background correction is required.

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Injection section of this manual.

Use the 10.0, 25.0 and 50.0 mg/L standards for instrument calibration.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, furnace alignment, lamp alignment, graphite tube, etc.).

2. Immediately after the calibration of the instrument, an initial calibration verification (ICV) standard of 12.5 ug/L and calibration blank (ICB) are to be analyzed. Thereafter, a continuing calibration verification (CCV) standard of 25.0 ug/L and a calibration blank (CCB) must be analyzed after every 10 analytical samples or after every 20 burns, whichever is more frequent. If less than 10 samples are analyzed, a CCV and CCB are still required. The last samples analyzed in the run are to be a CCV and CCB. These standards must be within 90-110% of the true value, or the analysis must be stopped, the problem corrected, the instrument recalibrated, and all samples following the last acceptable CCV are to be reanalyzed starting with a CCV and CCB.

3. Analyze a standard at, or less than, the contract required detection limit after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   a. If the spike recovery is within 85 - 115%, standard additions are not required.

   b. If the spike recovery is outside 85 - 115%, standard additions are required. (See Furnace Decision Tree for more detail.)

6. An EPA reference standard will be analyzed with each analysis.

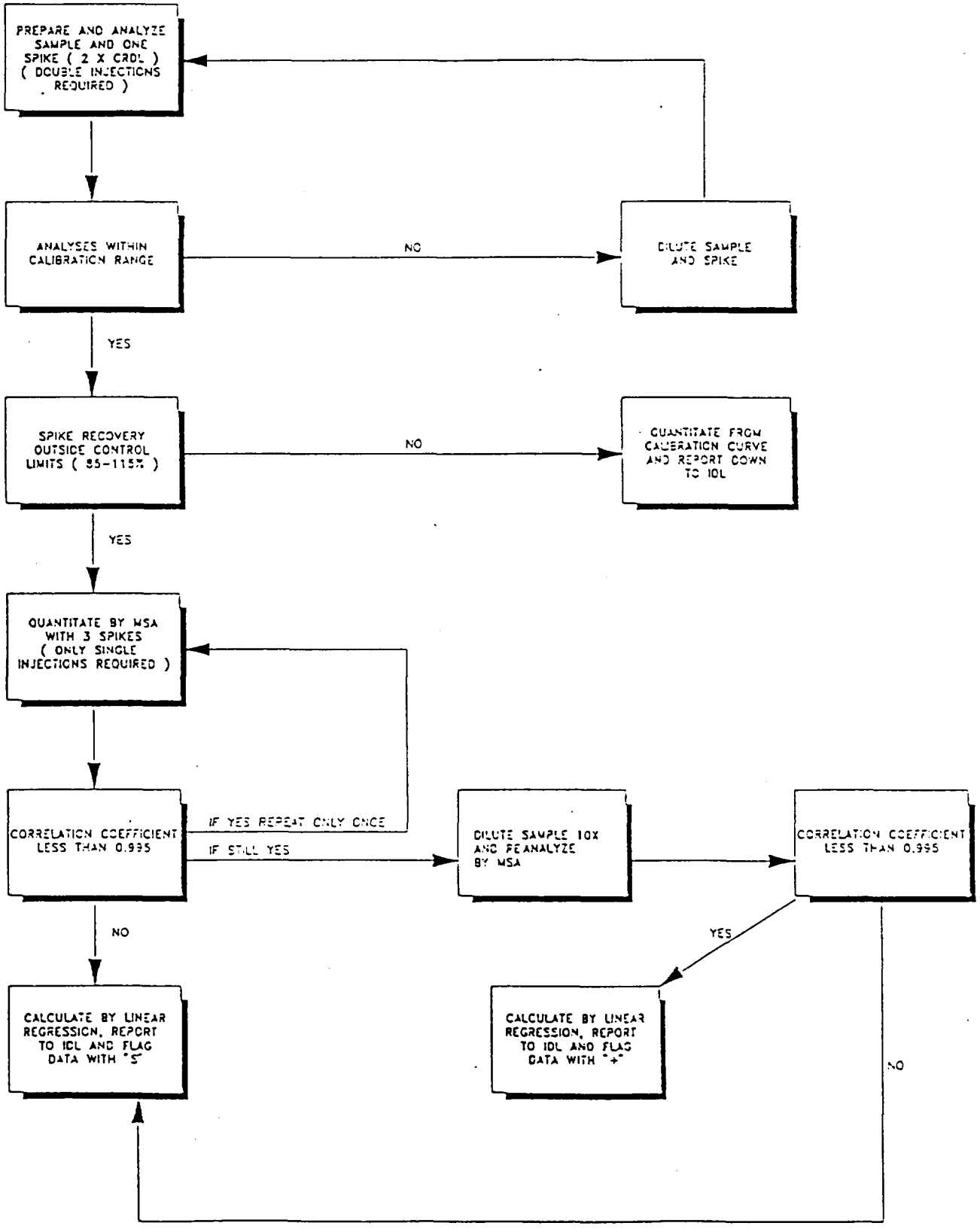
Calculations:

1. Calculate using instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

WARZYN

FURNACE CLP DECISION TREE



Effective Date: 4-28-92

VANADIUM-VARIAN 400

Method: AA - Furnace; Direct Injection

Reference: "Methods for Chemical Analysis of Water and Wastes", EPA 1984, Method 286.2

"Analytical Methods for Zeeman Graphite Tube Atomizers", Varian, 1986

"Statement of Work for Inorganic Analysis", ILM01.0, EPA 1990

Detection Limit: 0.002 mg/L

Optimum Range: 0.002 - 0.050 mg/L

Sample Handling: Acidify aqueous samples with nitric acid to pH <2. Analyze within 6 months. All samples must be digested prior to analysis.

Instrument Conditions:

Instrument Mode:	Absorbance
Calibration Mode:	Concentration
Measurement Mode:	Peak Area
Lamp Current (mA):	10
Slit Width (nm):	0.2
Slit Height:	Normal
Wavelength (nm):	318.5
Sample Introduction:	Sampler Premixed
Time Constant:	0.05
Measurement Time (sec):	1.0
Replicates:	2
Background Correction:	On
Maximum Absorbance:	1.80

FURNACE PARAMETERS

Hot inject samples at 95°C

Step	Temp (°C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	105	5.0	3.0	NORMAL	NO
2	130	12.0	3.0	NORMAL	NO
3	150	3.0	3.0	NORMAL	NO
4	1400	5.0	3.0	NORMAL	NO
5	1400	10.0	3.0	NORMAL	NO
6	1400	1.0	0.0	NORMAL	NO
7	2700	0.7	0.0	NORMAL	YES
8	2700	2.0	0.0	NORMAL	YES
9	2700	2.0	3.0	NORMAL	NO

Sample Volume: 20 uL

Calibration Standards: 10.0, 20.0, 50.0 ug/L.

Hot Inject: Yes, Temp. = 95°C

Graphite Tube Type: Pyrolytic coated partition tube

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. **Standard vanadium solution (1000 ug/L vanadium):** Pipet 1.0 mL of the 1000 ppm stock vanadium solution into a 1000 mL volumetric flask, add 0.5 mL HNO_3 and dilute to the mark with deionized water. Prepare fresh daily.

2. **Standards:** (Prepare fresh daily.)

Concentration of Standard	Volume of Vanadium Standard	Dilute to
10.0 ug/L	1.0 mL of 1000 ug/L V	100 mL
20.0 ug/L	2.0 mL of 1000 ug/L V	100 mL
50.0 ug/L	5.0 mL of 1000 ug/L V	100 mL

Notes:

1. Samples must be diluted to obtain concentrations within the optimum concentration range.

2. Standards are to be prepared in the same acid concentrations as the samples being analyzed.

3. The use of background correction is required.

4. The use of halide acids should be avoided.

5. Vanadium is a refactory metal, extra care should be taken that sample is not boiled during the digestion (vanadium is easily lost).

Procedure: For the analysis procedure, refer to the Atomic Absorption Spectrometry, Furnace - Direct Aspiration section of this manual.

Use the 10.0, 20.0 and 50.0 ug/L standards for instrument calibration.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, flame head alignment, lamp alignment, etc.)

2. Immediately after the calibration of the instrument, an initial calibration verification (ICV) standard of 20.0 ug/L and calibration blank (ICB) are to be analyzed. Thereafter, a continuing calibration verification (CCV) standard of 20.0 ug/L and a calibration blank (CCB) must be analyzed after every 10 analytical samples or after every 20 burns, whichever is more frequent. If less than 10 samples are analyzed, a CCV and CCB are still required. The last samples analyzed in the run are to be a CCV and CCB. These standards must be within 90-110% of the true value, or the analysis must be stopped, the problem corrected, the instrument recalibrated, and all samples following the last acceptable CCV are to be reanalyzed starting with a CCV and CCB.

3. Analyze a standard at, or less than, the contract required detection limit after the initial calibration verification and blank.

4. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges, or data must be flagged appropriately.

5. For every sample analyzed, an analytical spike (at the bench) must be run to verify that standard additions are not required. Criteria for standard additions are:

   - If the spike recovery is within 85 - 115%, standard additions are not required.

   - If the spike recovery is outside 85 - 115%, standard additions are required. (See Furnace Decision Tree for more detail.)

6. An EPA reference sample will be analyzed with each analysis.

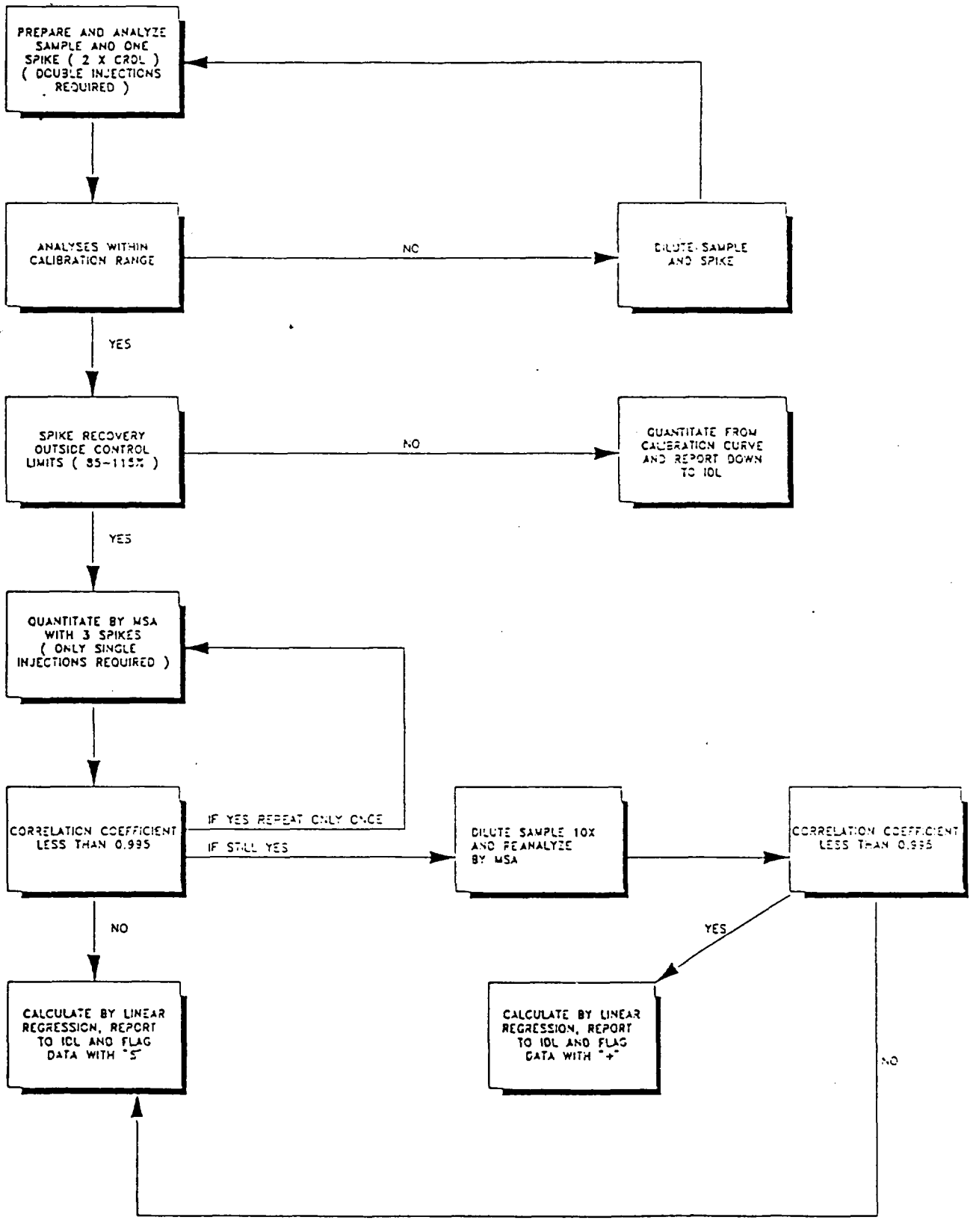
Calculations:

1. Calculate using instrument concentration mode, or

2. For method of standard additions calculate using linear regression.

WARZYN

FURNACE CLP DECISION TREE



Effective: 7-2-91

MERCURY DIGESTION LIQUID SAMPLES

Scope and Application: This mercury digestion method is applicable to drinking, surface, groundwater, domestic, and industrial wastewaters.

Method: Nitric/sulfuric acid digestion

Reference: EPA 1983, Method 245.1
"Statement of Work for Inorganic Analysis", ILM01.0, EPA 1990

Sample Handling: Preserve with concentrated HNO_3 to pH <2. Analyze within 28 days of sampling.

Reagents and Apparatus:

1. Water bath set @ 95°C
2. BOD bottles; 300 mL
3. Class A volumetric glassware
4. Instra-analyzed sulfuric acid
5. Instra-analyzed nitric acid
6. Potassium persulfate
7. Potassium permanganate
8. Sodium chloride
9. Hydroxylamine hydrochloride solution
10. Various Class A volumetric pipettes
11. Mercury stock and standard solutions

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. **Sodium chloride-hydroxylamine hydrochloride solution:** In a 1000ml volumetric flask dissolve 120.0 g of sodium chloride and 120.0 g of hydroxylamine hydrochloride in D.I. water, dilute to 1 liter.

2. **Potassium permanganate (5% solution, w/v):** In a 1000ml volumetric flask dissolve 50.0 g of potassium permanganate in D.I. water, dilute to 1 liter.

3. **Potassium persulfate (5% solution, w/v):** In a 1000ml volumetric flask dissolve 50.0 g of potassium persulfate in D.I. water, dilute to 1 liter.

4. **Intermediate mercury standard (10.0 mg/L):** Transfer 1.0 mL stock mercury (1000 mg/L) solution, plus 0.5 mL nitric acid, into a 100 mL volumetric flask and dilute to the mark with D.I. water. Prepare fresh daily!

5. **Working mercury standard (0.100 mg/L):** Transfer 1.0 mL of the 10.0 mg/L intermediate standard, plus 0.5 mL nitric acid, into a 100 mL volumetric flask and dilute to the mark with D.I. water. Prepare fresh daily!

Notes:

1. The mercury standards are volatile and unstable. Standards must be prepared daily.

2. Because of the toxic nature of mercury vapor, precaution must be taken to avoid inhalation. Vent the mercury vapor into an exhaust hood or pass the vapor through an absorbing media.

3. Hydroxylamine sulfate may be used rather than hydroxylamine hydrochloride.

4. All blanks, standards, and samples must be carried through the digestion procedure.

5. **Interferences:**

   a. Potassium permanganate is added to eliminate interferences from sulfide. Concentrations as high as 20 mg/L sulfide as sodium sulfide do not interfere.

   b. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have no effect on recovery of mercury from spiked samples.

   c. Seawaters, brines, and industrial effluents, high in chlorides, will require additional potassium permanganate. Care must be taken to ensure that the same amount of potassium permanganate is added to all samples, blanks, and standards so total volume remains constant.

Procedure:

All glassware is to be washed with soap and water, rinsed with tap water, acid rinsed with 10% HNO_3, and final rinsed with D.I. water.

Standard Preparation:

1. **The standard curve is to consist of the following standards:**

Standard Concentration
0.00 ug/L
0.50 ug/L
1.00 ug/L
5.00 ug/L
10.0 ug/L

2. Pipet 0, 0.5, 1.0, 5.0, and 10.0 mL aliquots of 0.10 mg/L working stock mercury solution to 300 mL BOD bottles.

3. Add D.I. water to bring volume to 100 mL and continue with the digestion procedure.

Sample Preparation:

1. Transfer 100 mL, or an aliquot diluted to 100 mL, to a 300 mL BOD bottle.

   To Spike: Pipette 1.0 mL of 0.10 mg/L mercury standard into the sample bottle.

Digestion:

1. Add 5 mL conc. sulfuric acid and 2.5 mL conc. nitric acid to each bottle. Mix by swirling.

2. Add 15 mL potassium permanganate solution to each bottle, mix by swirling. Allow to stand for at least 15 minutes. If the bottle does not remain purple in color, additional potassium permanganate is required. Equal volumes of potassium permanganate must be added to all bottles.

3. Add 8 mL of potassium persulfate solution to each bottle and heat for 2 hours in a water bath maintained at 95°C. Check the bottles periodically throughout the 2 hours to insure the samples remain purple. Add additional potassium permanganate, if needed, to all bottles in the digestion set.

4. Cool to room temperature.

5. Samples are now ready for analysis using the AA-cold vapor procedure.

Quality Control:

1. Refer to the cold vapor SOP for quality control requirements.

[rff-metcont-222]

Effective: 7-2-91

TOTAL MERCURY - AUTOMATED

Scope and Application: This method is applicable to digested drinking, surface, groundwater, domestic, and industrial wastewaters, soils, and sediments. All samples must be digested prior to analysis.

Method: Automated Cold Vapor

Reference: EPA 1984, Method 245.1, 245.5
SW846, 1982, Method 7471
"Vapor generation Accessory Operation Manual", Varian, 1984
"Statement of Work for Inorganic Analysis, No. 788", EPA 1989

Detection Limits: 0.20 ug/L

Optimum Range: 0.20-10.0 ug/L

Sample Handling: Samples should be kept capped until just prior to analysis.

Instrument Conditions:

Instrument Mode:		Absorbance
Calibration Mode:		Concentration
Measurement Mode:		Integration
Lamp Position:		1
Lamp Current (mA):		4
Slit Width (nm):	0.5	
Wavelength (nm):	253.7	
Flame:		Air only
Sample Introduction:		Auto Normal
Delay Time:		60
Time Constant:		0.05
Measurement Time (sec):		3.0
Replicates:		3
Background Correction:		On
Air Flow:	0.00	
Rinse Rate:		1
Rinse Time:		5.0
Recalibration Rate:		0
Reslope Rate:	0	

Reagents and Apparatus:

1. Varian SpectrAA20
2. Varian VGA-76 (cold vapor generator)
3. Varian PSC-56 (autosampler)
4. Sodium chloride
5. Hydroxylamine hydrochloride
6. Stannous chloride
7. Hydrochloric acid
8. Mercury lamp
9. Tygon tubing
10. Whatman #4 filter paper or equivalent

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. **Hydrochloric acid (20% v/v):** Add 100 mL of conc. HCl to 200 mL D.I. water in a 500 mL volumetric flask, dilute to 500 mL. **Prepare in the hood!**

2. **Stannous chloride (25% w/v):** Dissolve 125.0 g stannous chloride in 500 mL of 20% HCL. Prepare fresh every month.

3. **Sodium chloride-hydroxylamine hydrochloride solution:** Dissolve 120.0 g of sodium chloride and 120.0 g of hydroxylamine hydrochloride in D.I. water, dilute to 1 liter.

Notes:

1. Because of the toxic nature of mercury vapor, precaution must be taken to avoid inhalation. Vent the mercury vapor into an exhaust hood or pass the vapor through an absorbing media.

2. A 10% solution of stannous sulfate may be substituted for stannous chloride.

3. Hydroxylamine sulfate may be used rather than hydroxylamine hydrochloride.

4. **Interferences:**

   a. Potassium permanganate is added to eliminate interferences from sulfide. Concentrations as high as 20 mg/L sulfide as sodium sulfide do not interfere.

   b. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have no effect on recovery of mercury from spiked samples.

   c. Seawaters, brines, and industrial effluents, high in chlorides, will require additional potassium permanganate. during the oxidation step, chlorides are converted to free chlorine which also absorbs at the same wavelength as mercury.

d. Certain volatile organic materials that absorb at this wavelength may also cause an interference. A preliminary run without reagents can determine if this type of interference is present.

5. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by leaving digested mercury samples uncapped in the hood for approximately 30 minutes after the addition of the sodium chloride hydroxylamine solution, or allowing a prepared autosampler tray to stand 10-20 minutes before starting an automated analytical run.

6. If particulates remaining in the digested sample cause obstructions in the autosampler tubing, samples can be filtered through Whatman #4 filter paper, or its equivalent, after excess permanganate has been reduced.

Procedure:

For instrument set-up procedures, refer to the Atomic Absorption Spectrometry, Flame section of this manual.

For concentration mode, use 0.5, 1.0, 5.0 and 10.0 ug/L standards to calibrate the instrument.

A. **Cold Vapor System Set-up:**

1. Insert quartz cell in burner chamber. (Attaches to the air/acetylene burner head.)

2. Visually align cell, checking light path with a white card or paper.

3. Select "Optimization" page and adjust cell for maximum signal.

4. Replace pump tubing on vapor generator.

5. Fill reagent bottles with D.I. water and 25% SnCl (stannous chloride) solution as labelled.

B. **Sample Analysis:**

1. Prior to analysis, add 6 mL of the sodium chloride-hydroxylamine solution to each bottle to reduce the excess permanganate. Additional sodium chloride-hydroxylamine may be needed to discharge the purple color; equal volumes must be added to all bottles in the digestion set.

2. Pour approximately 12 mL of samples, standards, and blanks into sample tubes and arrange on the autosampler.

3. Turn on argon supply (46 psi recommended).

4. Turn on autosampler power.

5. Turn on vapor generator power (peristaltic pump will run continuously while power is on. Check reagent levels periodically during long runs).

6. Allow pump to operate for 3 to 4 minutes to stabilize flow rates.

7. Start automatic run.

8. Run will stop automatically after it is completed. Press "stop" to release computer.

9. Pull tubing ends out of reagents and let pump empty the lines. Power off pump and release pump tubing. Turn off argon supply.

10. Power off autosampler, printer and AA if done with analyses for the day.

Quality Control:

1. Establish a standard curve with the standards listed above plus a blank. Record the absorbance check standard in the absorbance check book. The absorbances should remain consistent from run to run. If not, necessary troubleshooting must be performed before continuing (check wavelength, tubing, lamp alignment, pump, etc.)

2. A quality control calibration check standard of 5.0 ug/L and a blank are to be analyzed initially and, at a minimum, after every 10 samples. If less than 10 samples are analyzed, a check standard and a blank are still required. The last samples analyzed in the run are to be the check standard and blank. These standards must be within acceptable ranges (80-120%) or the samples run after the last acceptable check standard are to be reanalyzed.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges or the data will be flagged appropriately.

4. An EPA or ERA reference standard will be analyzed with each analytical run. The reference standard must be within acceptable limits (80-120% of the true value) before any samples are analyzed.

Calculation:

1. Calculate using the instrument concentration mode, or

2. For method of standard additions, use linear regression.

[rff-metcont-225]

AUTOANALYZER

Scope and Application: Ions can be readily analyzed by a flow-injection autoanalyzer. The flow injection design gives the system excellent washout characteristics, to prevent carry over and cross contamination. The autoanalyzer is generally more sensitive and accurate than the manual wet-chemistry techniques.

Method: Flow injection

References: Lachat Instruments, 1986.

Sample Handling: See separate SOP's for requirements.

Reagents and Apparatus:

1. Lachat 3-channel autoanalyzer
2. Stock and standard ion solutions
3. Class A volumetric flasks
4. Class A volumetric pipets
5. Milli-Q water
6. Required interference filters
7. Disposable 4 mL cups
8. Automatic sampler
9. Proportioning pump
10. Injection module
11. Colorimeters
12. Manifolds
13. Columns - if needed
14. Helium gas
15. Computer
16. Printer

Procedure:

A. Instrument Set-Up

1. Depress red power switch on power strip located behind the computer terminal. This will turn on the computer, the screen, and the printer.

2. Depress red power switch on rear power strip on Lachat system.

3. Select manifold and make appropriate hydraulic connections.

   Hydraulic connections:

a. Use correct sample loop length to connect. Lines 1, 4.

b. Line 2 is carrier line.

c. Line 3 goes to manifold.

d. Line 5 goes to waste container.

e. Line 6 comes from sample probe.

f. Connect manifold to flow through cell.

Tension levers should be up when pump tubing is inserted. Snap pump tubing cartridges into place.

4. Insert correct filter.

5. Pump Milli-Q water through lines for 5 minutes by depressing the pump ON button. Check for leaks.

6. Computer - At the C> type in "quikcalc". This calls up the Lachat software and puts you at the master menu. Press <enter>.

7. Put lines into reagents and/or degassed Milli-Q water.

8. Computer - Select "Load/Stop Background Method" on the master menu. Press <enter>.

9. Select appropriate method. Press <enter>.

10. Printer should be set at FONT 0.

11. Pump reagents until a steady baseline is achieved.

12. When using a method with a column (SO_4 or NO_3), the column may be inserted at this point. See method SOP's for more details.

13. For each analytical channel, adjust zero knob so that the baseline is near the bottom of the screen (between .000 - .030).

14. Adjust gain while injecting top standard.

    a. Place autosampler probe into the highest standard bottle.

    b. After 20-30 seconds, press cycle button on front panel so that LED light is red. This is the load position.

    c. After 25 seconds (or less depending on sample loop size), press cycle button so that LED light is green. This is the inject position.

d. Adjust gain knob on detector so that peak reading on the colorimetric is 1.700-1.950.

e. Repeat until gain is properly adjusted.

f. Wipe probe and replace the autosampler probe into the sampler.

15. Select menu item by going into foreground. (Press and hold Alt key, then press Esc key).

    a. Select "Sample Tray Information and Start Analysis" on master menu. Press <enter>.

    b. Press <enter> or type in sample tray reference number if it is a tray which has already been typed in.

    c. Enter tray ID and operator. Check "Display Standards Position in Tray" to insure the tray is set-up properly.

    d. Select "Enter Sample ID's". Press <enter>.

    e. Type in sample information. Check standards will automatically be placed in the tray information portion.

    f. Press Esc once to return to menu.

16. Put tray with samples in appropriate cup locations on autosampler. Position try to the cup containing standard A (usually #35 or so). Select "Start Analysis." Press <enter>.

17. The second screen will ask if the tray has standards or not. If you standardized the first tray of the run and all the check standards are within QC ranges, recalibration for the next tray is <u>not</u> necessary. Select appropriate option. Press <enter>.

18. Press Alt, Esc keys together, to get back to background to view the calibration peaks.

    After calibration is complete:

    - go into the foreground (Press Alt, Esc keys)
    - select "display calibration graph" (Press <enter>)
    - review the data
    - return to the background (Press Alt, Esc keys)

- press "G" for good calibration. Analysis will continue.

- press "R" for re-calibration. Remember to refill standard cups and reposition sample tray before pressing "R"!

B. Instrument Shut-Down

1. Press Alt/Esc keys to get to the foreground. Select "Load/Stop Background Method". Press <enter>. To question-"Stop background (Y/N)?" Press "Yes". Press Esc key to return to main menu.

2. If column is used, stop the pump and disconnect from manifold.

3. Pull lines from reagents into a wash beaker of D.I..

4. Pump D.I. through lines for 2-5 minutes.

5. Pump air through lines until manifold is dry.

6. Turn off pump.

7. Release tubing cartridges and lower tension levers. Release tubing.

8. Turn off main switch on rear power strip.

9. Empty and rinse waste containers, if necessary.

10. Perform back-up on current data files, once a week. (See Section C)

11. Turn off the computer and printer.

C. Backing-up the Data Files

1. Exit to DOS

2. At C> Type: cd\fialab\data Press <enter>

3. At C> Type: copy *.rpt a: Press <enter>
After everything is copied - remove disc.

4. At C> Type: del *.* Press <enter>

5. Are you sure (Y/N)? Type: Y Press <enter>

6. At C> Type: cd\ Press <enter>

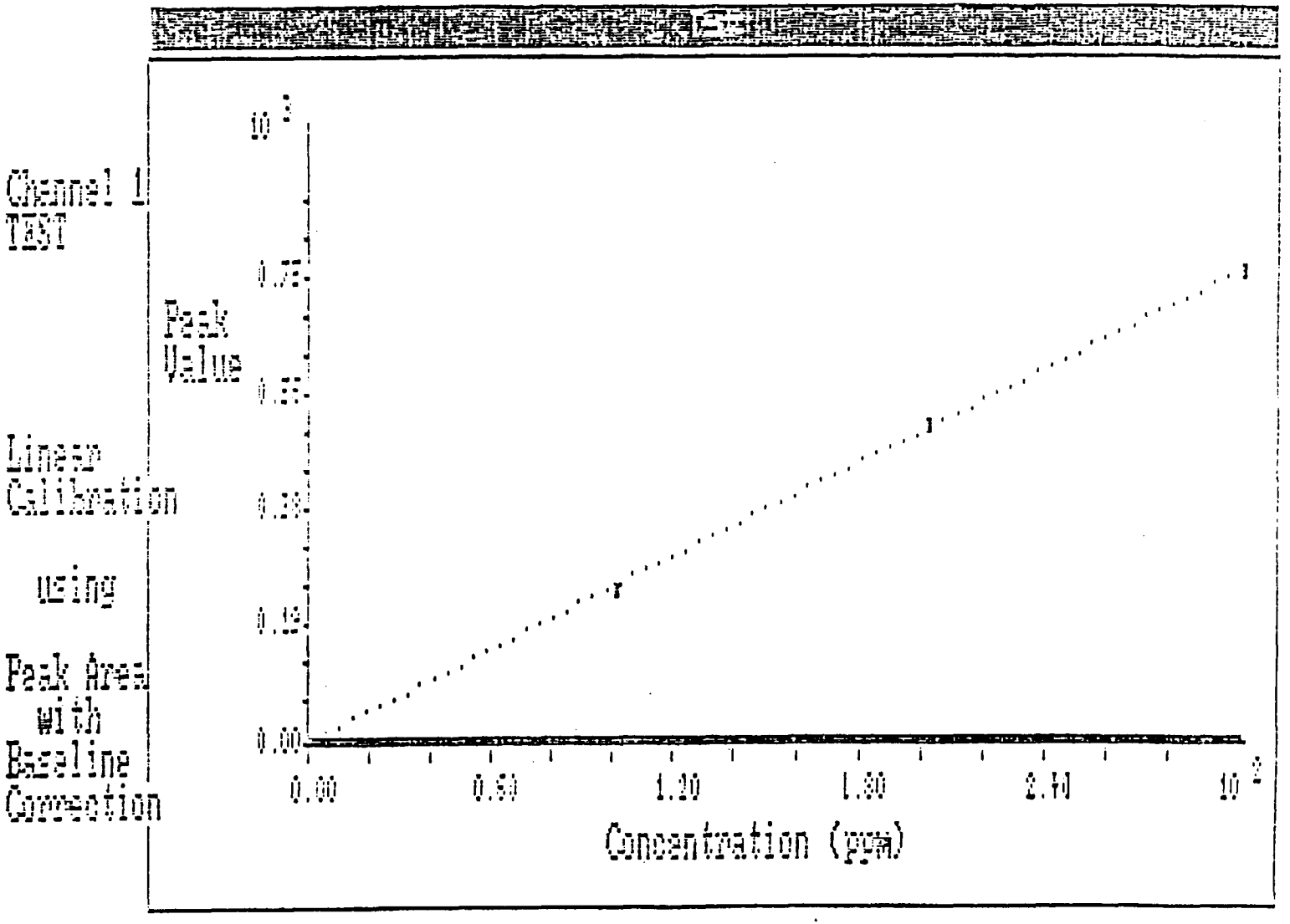
7. Turn off the red switch on the computer power strip to turn off the computer, printer and screen.

D. Quikchem Calibration

QuikCalc II uses a calibration technique called multisegment linear fitting which gives extensive flexibility to the user. It allows the calibration curve to be defined in terms of individual linear segments which can span each of several standards. Following processing of the calibration standards, a correlation coefficient is calculated for each segment with more than two standards or replicates. It provides important statistical information about each segment and gives the user a high degree of confidence in the determined sample values. See Figure 1.

Qu''ale II Calibration

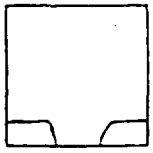
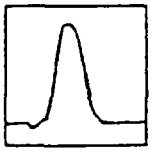
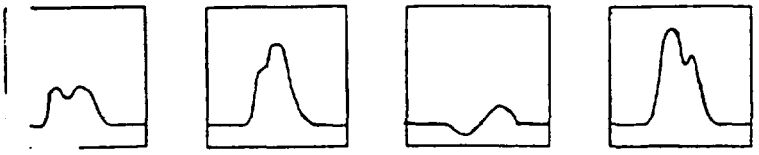
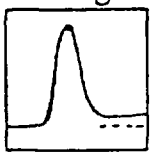
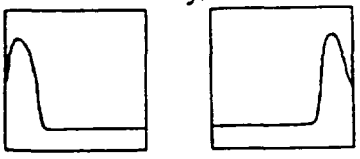
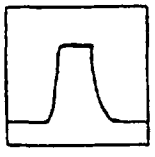
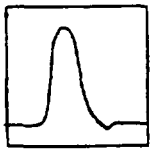
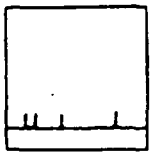
FIGURE 1



Correlation Coefficient: 0.99925

Press the [Esc] key to continue.

LACHAT TROUBLESHOOTING GUIDE

Problem:	Cause:
Negative peak 	1. Contaminated carrier 2. Bad or no SO_4 column or sample extremely high in hardness 3. Samples high in oxidizing agents
Reproduceable dip when valve switches (before peak) 	1. Bad color reagent 2. Could also be valve turning artifact caused by a highly colored reagent
Odd looking peaks 	1. Index of refraction problem, matrix related (usually acid or pH buffering) 2. Also method interferences: high hardness on SO_4 method, oxidizing samples on nitrate method 3. Bad reagents
Shifting baseline 	1. Flow problem 2. Precipitate build-up on SO_4 manifold tubing
Peak too early/late 	1. Usually flow problem 2. Valve not set to an initial load position state before starting run 3. Incorrect pump setting or other timing problem
Peak cut off in window 	1. Reagents exceeded-reagents improperly prepared 2. Standards incorrectly prepared
Reproduceable dip after peak 	1. Bad column
Small intermittent peaks 	1. Milli-Q or reagents not degassed properly or adequately 2. Waste line coil not installed (for the methods which require it)

Three basic areas of troubleshooting:

1. Fluidics (clogs, old pump tubing, crimp in manifold tubing)
2. Chemistry
3. Timing (not usually a problem after initial development)

BLH/rff
[rff-genpol-604]

Effective Date: 5.24.91

CYANIDE, TOTAL - DISTILLATION

Scope and Application: This method is applicable to the determination of cyanide in drinking water, surface water, ground-water, sludges, soils and industrial wastes.

Methods: Distillation, Automated Colorimetric

Reference: EPA 1983, Method 335.2,
SW-846, Method 9012
Standard Methods, 16th Edition, Method 412

Detection Limit: 0.005 mg/L

Optimum Range: 0.005 - 0.400 mg/L

Sample Handling: Preserve with sodium hydroxide to pH > 12 and refrigerate at 4°C
Analyze samples within 12 days of receipt date.

Reagents and Apparatus:

1. Cyanide reflux distillation apparatus
2. 25 mL and 50 mL graduated cylinders
3. Vacuum pump
4. Heating mantle
5. 250 mL volumetric flasks
6. Sodium hydroxide
7. Sulfuric acid, concentrated
8. Magnesium chloride
9. Deionized water
10. Bismuth nitrate
11. Sulfamic acid
12. Acetic acid, concentrated
13. Sodium thiosulfate, crystals

Reagent Preparation: (Prepare fresh every 6 months, unless otherwise noted.)

1. **Sodium hydroxide (1.25N):** Dissolve 50.0 g NaOH in D.I. water and dilute to 1 liter in a volumetric flask. Store in a plastic bottle.

2. **Magnesium chloride solution:** Dissolve 510.0 g $MgCl_2 \cdot 6H_2O$ in D.I. water and dilute to 1 liter. Store in a plastic bottle.

3. **Stock cyanide solution (1000 mg/L):** Dissolve 0.6275 g KCN and 0.5 g KOH and dilute to 250 mls with D.I. water in a volumetric flask. Prepare fresh every month. **Caution: Toxic!** Refrigerate.

4. **Standard cyanide solution (5 mg/L):** Pipet 5 mL of stock cyanide solution into 1 L volumetric flask containing approximately 500 mL D.I. water and 2 mL of 10N NaOH as a preservative. Dilute to volume with DI water. **Prepare fresh daily.** Refrigerate.

5. **Bismuth nitrate solution:** Dissolve 30.0 g of $Bi(NO_3)_3$ in 100 mL of D.I. water. While stirring, add 250 mL of concentrated acetic acid. Stir until dissolved. Dilute to 1 liter with D.I. water.

6. **Sulfamic acid solution:** Dissolve 40.0 g of sulfamic acid in D.I. water. Dilute to 1 liter.

Notes:

1. **Caution:** Use care in handling of samples with cyanide because of the toxicity. Avoid skin contact, inhalation, or ingestion. **Always have a respirator on when doing this test.**

   If a sample begins to bump or back up the tube, quickly increase the flow rate, and turn the heat down (or off) until bumping subsides.

   If a sample does boil over, proceed as follows:

   - Pull inlet tube out
   - Turn heat off (For your protection, use gloves.)
   - Put sample and heating mantle into hood
   - When sample is cool remove from mantle and heat mantle in hood on high until acid fumes have dissipated.

2. Oxidizing agents, such as chlorine, interfere by decomposing cyanides. If chlorine is believed to present, put a drop of sample on potassium iodide starch paper. If paper turns bluish, add a few crystals of sodium thiosulfate ($Na_2S_2O_3$) to the sample, mix, and retest. Continue adding sodium thiosulfate until free from chlorine. Then, add 0.1 g sodium thiosulfate in excess.

3. Sulfides interfere by forming thiocyanate at a high pH. If sulfides are believed to be present, put a drop of sample on lead acetate test paper treated with acetic acid buffer solution at ph4. Darkening of paper indicates sulfides. If sulfides are present, add 50 mL of bismuth nitrate solution after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4.

   Alternatively, $Cd(NO_3)_2 \cdot 4H_20$, $CdCO_3$ or $PbCO_3$ can be added after the distillation, but prior to color development. Bismuth nitrate added prior to the distillation process is the preferred choice.

4. Fatty acids, high carbonates, and aldehydes can interfere. Refer to Standard Methods for troubleshooting.

5. High concentrations of NO_3 and NO_2 can give false positive results. If samples contain high concentrations of NO_3 and/or NO_2, add 50 mL of sulfamic acid solution after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4.

6. Do not use bismuth nitrate and sulfamic acid aon the same sapmle. Pretreatment with both results in poor (bias low) cyanide recovery.

Procedure:

1. All glassware is to be soap and water washed, tap rinsed, and deionized rinsed prior to analyses. Dichromate or acetone may also be used to clean the glassware prior to the soap and water wash.

2. Connect and set up cyanide reflux distillation apparatus as shown in Figure 2.

3. Prepare the 0.100 mg/L cyanide digestion standard as follows:

   Add 5 mL of the 5 mg/L cyanide solution to 250 mL of DI water. (Prepare in the distillation flask.)

4. Pour 250 mL of sample into cyanide distilling flask. If a solid or semi-solid sample is to be analyzed, use a 1.0 g sample size and add 250 mL of D.I. water to the distilling flask. (Record the amount of sample used.) Add an additional 250 mL D.I. water for a total volume of 500 mL in the distillation flask. Add 3-5 boiling chips.

   To Spike: Add 5 mL of the 5 mg/L cyanide solution to the 250 mL of sample for a final concentration of 0.100 mg/L.

5. Using a graduated cylinder, add 50 mL 1.25 N sodium hydroxide to the absorber tube and connect.

6. Turn on vacuum pump and adjust so that one bubble per second enters the distillation flask through the air inlet tube.

7. Slowly add 25 mL concentrated sulfuric acid through the air inlet tube. Rinse the tube with D.I. water and wait for about 2-3 minutes, until the sulfuric acid has been dispersed into the sample.

8. Using a graduated cylinder, add 20 mL magnesium chloride solution into the air inlet tube and rinse the tube with D.I. water.

9. Turn heating mantle on to setting of 10 till sample boils (approximatley 15 minutes). Watch vacuum rate carefully and adjust as necessary maintaining a rate of one bubble per second. As temperature increases, bubbling increases, and the solution can be drawn from the absorption tube or blown out the air inlet tube.

10. After sample starts boiling, turn heating mantle down to 6-7. **Watch vacuum rate carefully and adjust as necessary** maintaining a rate of one bubble per second. Reflux for one hour.

11. Turn off heat and continue vacuum for 15 minutes.

12. Remove inlet tubes.

13. Disconnect absorber, DI rinse absorber top into absorbing solution, and shut off vacuum pump.

14. Pour solution from absorber tube into a 250 mL volumetric flask. Using D.I. water, rinse the absorption tube (3 times) and add to the volumetric flask. Dilute to mark with DI water. Mix by inverting.

15. Distillates are ready for analysis. Proceed with Lachat SOP CNAAHC for the automated colorimetric step.

Quality Control:

1. The standard curve does not need to be carried through the distillation procedure.

2. A reagent blank is to be analyzed with each set of samples. This blank is to be carried through the distillation steps as a check for contamination.

3. A quality control distilled check standard of 0.100 mg/L cyanide is to be analyzed with each set of samples. This standard is to be carried through the entire procedure including the distillation step.

4. A known reference standard (LCS) is to be analyzed with each set of samples. This standard is to be carried through the entire procedure including the distillation steps. This standard must be within 80-120% of the true value and within 95% confidence limits (if available) or the samples are to be reanalyzed.

5. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicate results are to be within acceptable ranges.

6. Aqueous and solid/semi-solid samples are separate matrices. Duplicates and spikes are required for each matrix type.

Calculation:

1. Calculate distillate concentration with Lachat QuikChem software, in the concentration mode, using the IBM XT computer. (Be sure to calculate in any distillation dilution into the final result.)

$$\text{ug/L CN} = \frac{(\text{distillate volume,mL})(\text{distillate concentration,mg/L}) \times 1000}{(\text{sample volume,mL})}$$

$$\text{mg/kg CN} = \frac{(\text{distillate volume,mL})(\text{distillate concentration,mg/L})}{(\text{sample weight,gm})}$$

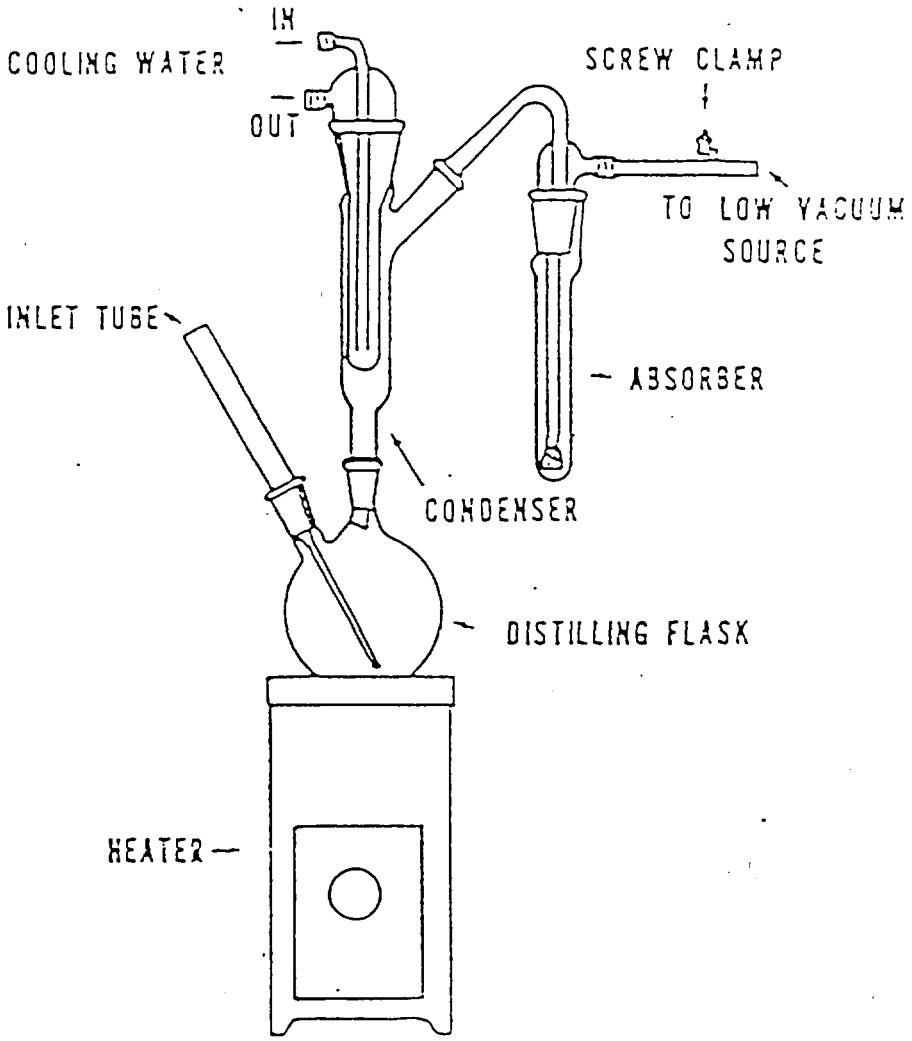


FIGURE 2

CYANIDE DISTILLATION APPARATUS

Effective Date: 7-2-91

TOTAL CYANIDE - AUTOANALYZER - (HEATED METHOD)

Scope and Application: This method is applicable to **distilled** groundwater, drinking water, wastewater, sediments and soils. All samples must be distilled prior to analysis with the autoanalyzer. (Refer to SOP # CNDISC.)

Reference: EPA, 1983, Method 335.3
Lachat Instruments, 1990, Method 10-204-00-1-A
Standard Methods, 16th Edition, pages 337-338
SW-846, Method 9012
SOW No. 788 including Rev 2/89 and 6/89

Instrument Detection Limit: 0.005 mg/L

Optimum Range: 0.005 - 0.400 mg/L

Sample Handling: Samples should be capped and refrigerated at 4°C after distillation. Samples must be analyzed within 3 days after distillation and within 12 days of receipt date.

Instrument Conditions:

1. Pump speed: 35
2. Cycle period: 50 seconds
3. Load period: 20 seconds
4. Inject period: 15 seconds
5. Inject to start of peak period: 30 seconds
6. Inject to end of peak period: 78 seconds
7. Gain: 420
8. Zero: 350
9. Interference filter: 570 mm
10. Sample loop: 150 cm (0.80 mm i.d.)
11. Standards for calibration: 0, 0.010, 0.020, 0.100, 0.200, 0.400 mg/L
12. Water Bath 45°C (Position A).

Reagent Preparation: (Prepare fresh every 6 months unless otherwise noted.)

1. **Degassed Milli-Q-water - 2 options:**

   a. Boil Milli-Q water vigorously for 5 minutes. Cool and store in cubitainer.

   b. Bubble helium, using the fritted gas dispersion tube, through 20 L Milli-Q water for 15-20 minutes. Store in cubitainer.

2. **Carrier - 0.25N NaOH:** In a 1 L volumetric flask, dissolve 10.0 g NaOH in 900 mL DI water. Dilute to the mark and invert several times. Filter through 0.45 micron filter paper. Store in a plastic bottle.

3. **Phosphate buffer - 0.71 M:** In a 1 L volumetric flask, dissolve 97.0 g anhydrous potassium dihydrogen phosphate (potassium phosphate, monobasic, anhydrous, KH_2PO_4) in 800 mL degassed MQ water. Add 8.1 mL concentrated (85%) phosphoric acid. Dilute to the mark with degassed MQ water and invert several times.

4. **Chloramine-T solution:** In a 500 ml volumetric dissolve 2.0 g of chloramine-T in degassed Milli-Q. Dilute to the mark and invert several times. Prepare fresh weekly and store refrigerated.

5. **Pyridine - barbituric acid reagent:** In the fume hood, place 15.0 g barbituric acid in a 1 L beaker and add 100 mL of degassed MQ water, rinsing down the sides of the beaker to wet the barbituric acid. Add 75 mL pyridine (C_5H_5N) while stirring with a stir bar. Mix until barbituric acid dissolves. Add 15 mL concentrated HCl and stir. Transfer to a 1 L volumetric flask, dilute to the mark with degassed MQ water and invert several times. Refrigerate. Prepare fresh every 2 months.

6. **Stock cyanide solution (1000 mg/L):** Dissolve 0.6275 g KCN and 0.5 g KOH and dilute to 250 mL with D.I. water in a volumetric flask. Prepare fresh every month. Refrigerate. **Caution: Toxic!**

7. **Standard cyanide solution (5.0 mg/L):** Pipet 5 mL of stock cyanide solution into 1 L volumetric flask, add approximately 500 mL DI water. Add 2 mL of 10N NaOH as a preservative and dilute to volume with DI water. Prepare fresh daily. Refrigerate.

8. **Cyanide standards:** Prepare by pipetting the volumes noted below into 250 mL volumetric flasks, adding 50 mL of 1.25N NaOH, and diluting to the mark with degassed MQ water. (The 1.25N NaOH must be added - very important!) **Prepare fresh daily.**

Concentration of Standard	Letter Identifier	Volume of 5.0 mg/L working standard (ml)	Dilute to
0.000 mg/L	A	0 mL	250 mL
0.010 mg/L	B	0.5 mL	250 mL
0.020 mg/L	C	1.0 mL	250 mL
0.100 mg/L	D	5.0 mL	250 mL
0.200 mg/L	E	10 mL	250 mL
0.400 mg/L	F	20 mL	250 mL

Note: Computer refers to standards by letter.

Notes:

1. This chemistry is temperature sensitive. The heated method reduces or eliminates sensitivity drift due to temperature changes.

2. Use wasteline coil to help eliminate air spikes.

3. Any sample dilutions must be diluted with 0.25N NaOH, **not** water. You may use the carrier or the zero standard for this.

4. Interferences are reduced or eliminated by the distillation procedure. Cyanide analyses suffer from many interferences. See EPA and Standard Methods references for detailed discussion. Information and recommendations for the manual pyridine-barbituric acid color development also apply to this automated method.

5. Samples must be diluted to obtain concentrations within the optimum working range.

6. The gain and zero settings are guidelines and must be optimized each day.

7. Color is an interference, dilute the sample and also manually spike the dilution to confirm the quality of the result.

System Operation:

1. Refer to "Auto Analyzer Operation Start-up Procedure" (IOP# LAAC-Section A).

2. Analyze an initial calibration check standard, a blank, a distilled known reference standard, a distilled standard and a distilled blank at the beginning of each run. The blanks must be below the detection limit and the standards must be within required control limits before any samples are analyzed.

3. Spikes are be distilled at a level of 0.100 mg/L.

4. The calibration check standard is 0.100 mg/L (D).

5. The distilled standard is 0.100 mg/L.

6. If a sample and spike are **overrange:**

   a. Dilute the sample and spike if dilution ≤ 1:5. The distilled spike should be detectable.
   b. Dilute the sample, spike and analyze a manual spike if dilution > 1:5.

7. Refer to Auto Analyzer shut-down procedure. (IOP# LAAC-Section B).

Quality Control:

1. Establish a standard curve with the standards listed above. The derived concentrations for each calibration standard must read within 10% of the true value. The derived value for the blank must be less than the method detection limit.

2. A quality control calibration check standard of 0.100 mg/L (D) and a blank are to be analyzed initially and at a minimum, after every 10 samples. If less than 10 samples are analyzed, a calibration check standard and blank are still required. The last samples analyzed in the run are to be the calibration check standard and blank. These standards must be within the acceptable ranges and blanks must be below the method detection limit or the samples run after the last acceptable calibration check standard and blank are to be reanalyzed.

3. Duplicate and spike a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate and spike are still required. Spike recoveries and duplicates are to be within acceptable ranges or data must be flagged appropriately. (These samples must be carried through the distillation step.)

Calculations:

1. Calculate with Lachat QuikChem software, in the concentration mode, using the IBM XT computer. Be sure to calculate any digestion dilution into the final result.

APPENDIX B-12

LANDFILL GAS VOCS (ENSECO)

Enseco - Air Toxics Laboratory
18501 East Gale Avenue, Suite 130
City of Industry, CA 91748-1321
(818) 965-1006 • FAX (818) 965-1003

Enseco
A Corning Company

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The above statement relates to the following attached confidential Enseco documents:

SOP NO. CRL-LM-7001
"The Determination of Volatile Organics (VOCs) in Ambient Air by GC/MS - Scan Mode"

STANDARD
OPERATING
PROCEDURE

Subject or Title:

The Determination of Volatile Organics (VOCS)
in Ambient Air by GC/MS - Scan Mode

SOP NO:	Revision No.: 2.0	Effective Date:
CRL-LM-7001		March 1, 1990

Supercedes: Revision 1.0

1. Scope and Application

1.1 Analytes (See Table 1)

1.2 Detection limit (See Table 1)

1.3 Applicable matrices - air

1.4 Dynamic range (See Table 1)

1.5 Approximate analytical time

4 min. - cool down of cryo trap
2 min. - flush of inlet system on trap
10 min. - collection of 500 mL sample on trap
2 min. - flush of inlet system with internal std.
2 min. - collection of 100 mL of internal std on trap
2 min. - flush of trap with HP Helium
32 min. - GC run time

When running multiple samples, steps can be overlapped to reduce run time to 40 min.

Prepared by: Steve Harris	Date: 6/04/90
Management Approval:	Date: 6/04/90
QA Officer Approval: Paul Christ	Date: 6/5/90

TABLE 1. VOC Target Compounds

	Compound	R.T.	Detection Limits MDL (ppbv)	Dynamic Range (ppbv)
2)	Dichlorodifluoromethane (Freon 12)	1.49	0.87	0.87-300
3)	Chloromethane	2.48	1.2	1.2-300
4)	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	2.52	1.0	1.0-300
5)	Vinyl chloride	2.86	1.2	1.2-300
6)	Bromomethane	3.58	1.5	1.5-300
7)	Chloroethane	3.93	2.5	2.5-300
8)	Trichlorofluoromethane (11)	4.54	0.55	0.55-300
9)	cis-1,2-Dichloroethene	5.63	0.84	0.84-300
10)	Carbon disulfide	5.63	6.2	6.2-1200
11)	1,1,2-Trichloro- 1,2,2-trifluoroethane (Freon 113)	5.87	0.96	0.96-300
12)	Acetone	6.10	6.6	6.6-300
14)	Methylene chloride	6.89	1.9	1.9-300
15)	trans-1,2-Dichloroethene	7.36	1.9	1.9-300
16)	Hexane	7.98	4.0	4.0-300
17)	1,1-Dichloroethane	8.22	1.2	1.2-300
18)	Vinyl Acetate	8.71	1.3	1.3-300
19)	1,1-Dichloroethene	9.43	1.1	1.1-300
20)	2-Butanone	9.68	1.4	1.4-300
21)	Chloroform	10.27	1.1	1.1-300
22)	1,1,1-Trichloroethane	10.27	0.45	0.45-300
23)	Carbon tetrachloride	10.53	0.55	0.55-300
24)	Benzene	11.00	1.6	1.6-300
25)	1,2-Dichloroethane	11.19	0.53	0.53-300
26)	Trichloroethene	12.44	1.2	1.2-300
27)	1,2-Dichloropropane	12.87	3.9	3.9-300
28)	1,4-Dioxane	13.34	3.5	3.5-300
29)	Bromodichloromethane	13.68	0.90	0.90-300
30)	cis-1,3-Dichloropropene	14.61	1.5	1.5-300
31)	4-Methyl-2-pentanone	15.14	1.6	1.6-300
32)	Toluene	15.16	1.5	1.5-300
33)	trans-1,3-Dichloropropene	16.00	1.6	1.6-300
34)	1,1,2-Trichloroethane	16.34	1.4	1.4-300
35)	Tetrachloroethene	16.28	1.4	1.4-300
36)	2-Hexanone	17.10	3.0	3.0-300
37)	Dibromochloromethane	17.06	1.4	1.4-300
38)	1,2-Dibromoethane	17.08	1.0	1.0-300
39)	Chlorobenzene	18.28	1.3	1.3-300
40)	Ethylbenzene	18.73	1.3	1.3-300
41)	1,4-and 1,3-(p,m) Xylene	19.04	2.6	2.6-600

TABLE 1. VOC Target Compounds
(Continued)

	Compound	R.T.	Detection Limits MDL (ppbv)	Dynamic Range
42)	1,2-(ortho) Xylene	19.94	1.1	1.1-300
43)	Styrene	20.02	3.5	3.5-300
44)	Bromoform	20.37	1.0	1.0-300
45)	1,1,2,2-Tetrachloroethane	21.99	1.9	1.9-30
46)	Benzyl chloride	21.90	1.0	1.0-30
47)	4-Ethyltoluene	22.31	2.0	2.0-300
48)	1,3,5-Trimethylbenzene	22.48	1.3	1.3-300
49)	1,2,4-Trimethylbenzene	23.37	1.5	1.5-300
50)	1,3-Dichlorobenzene	23.04	1.7	1.7-300
51)	1,4-Dichlorobenzene	24.13	2.2	2.2-300
52)	1,2-Dichlorobenzene	24.97	2.4	2.4-300
53)	1,2,4-Trichlorobenzene	29.28	3.6	3.6-300
54)	Hexachlorobutadiene	29.93	2.4	2.4-300

2. Summary of Method

2.1 A pressurized air sample is metered through a mass flow controller onto a cryogenically cooled trap. After 500 mL of the sample has been trapped, a valve is switched and the trap is heated to purge the trap's contents onto the gas chromatography column. The target compounds are analyzed with a mass spectrometer operated in the scan mode.

3. Comments

3.1 Interferences

3.1.1 Gas regulators are cleaned by the manufacturer using Freon 113, which is one of the target compounds. Before using ultra high purity (UHP) Nitrogen (N_2), Hydrocarbon (HC) free air, Internal Standard (I.S.), or a target compound standard mix, each regulator should be purged a minimum of three times with the appropriate gas.

3.1.2 Contamination may occur in the sampling system if canisters are not properly cleaned prior to use. Canisters used to collect source samples should not be used for the collection

of ambient air samples until a blank analysis indicates that no target compounds are present above the MDL. All other sampling equipment including pumps, flow controllers and filters must be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples.

3.2 Helpful Hints

None

4. Safety Issues

4.1 In order to prevent contamination of the lab air by the samples, the vent line must be connected to the system outlet and the fume hood must be on.

4.2 While making standards, the fume hood must be running. When finished valves must be closed and lines vented.

4.3 All compressed gas cylinders must be securely fastened to a bench or wall.

4.4 Normal precautions should be used in the handling of liquid nitrogen (LN_2) (do not touch transfer lines as burns can result).

4.5 Sampling canisters should never be pressurized over 40 psig.

5. Sample Collection, Preservation, Containers and Holding Times

5.1 Samples should be collected in precleaned and batch analyzed SUMMA passivated canisters. A 7 micron filter should be placed on the inlet of the can to protect the valve from particulates. Canisters should never be pressurized over 40 psig.

5.2 The absolute pressure of the canister must be recorded before and after sample collection.

5.3 Samples must be kept at <25°C.

5.4 Samples should be analyzed within 14 days of collection.

6. Apparatus and Materials

6.1 Gas chromatograph - capable of subambient temperature programming for the oven and with the jet separator option (Hewlett Packard 5890).

6.2 Mass-selective detector - equipped with computer and appropriate software (Hewlett Packard 5970B with HP-1000 RTE-A data system).

6.3 Cryogenic trap with temperature control assembly (Nutech 8533). See Figure 1.

6.4 Electronic mass flow controller - for maintaining constant sample flow (Unit Instruments)

6.5 Chromatographic grade stainless steel tubing and stainless steel plumbing fittings.

6.6 Chromatographic column - DB-624 0.53 ID, 30 meter length (J&W Scientific).

6.7 Stainless steel vacuum/pressure gauge capable of measuring from 30" of mercury (Hg) to 40 psig. (Span Instruments)

6.8 High precision vacuum gauge - for making daily standards. (Wallace & Tiernan Pennwalt)

6.9 Pressure regulators for carrier gas and standards - 2 stage, stainless steel diagram.

6.10 SUMMA passivated canisters 6 L (Scientific Instrumentation Specialists)

6.11 7 micron filters (Nupro), or equivalent.

7. Reagents and Standards

7.1 4-bromofluorobenzene, 50 ng/mL in methanol (for tuning of mass spectrometer).

7.2 High purity helium for carrier gas.

7.3 Standards at a nominal concentration of 1 ppmv (CS_2 is not as stable and so the concentration is 5 ppmv). Standards are prepared in a balance gas of nitrogen and are analytically certified by the supplier (Scott-Marrin and Scott Specialty). To facilitate certification by vendor, the standards were divided into 5 cylinders. (See Tables 2-7.)

7.4 Internal standard mix of bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d5 at 1000 ug/ml each in methanol (Supelco). (See Table 6.)

FIGURE 1. Nutech 8533 Flow Diagram

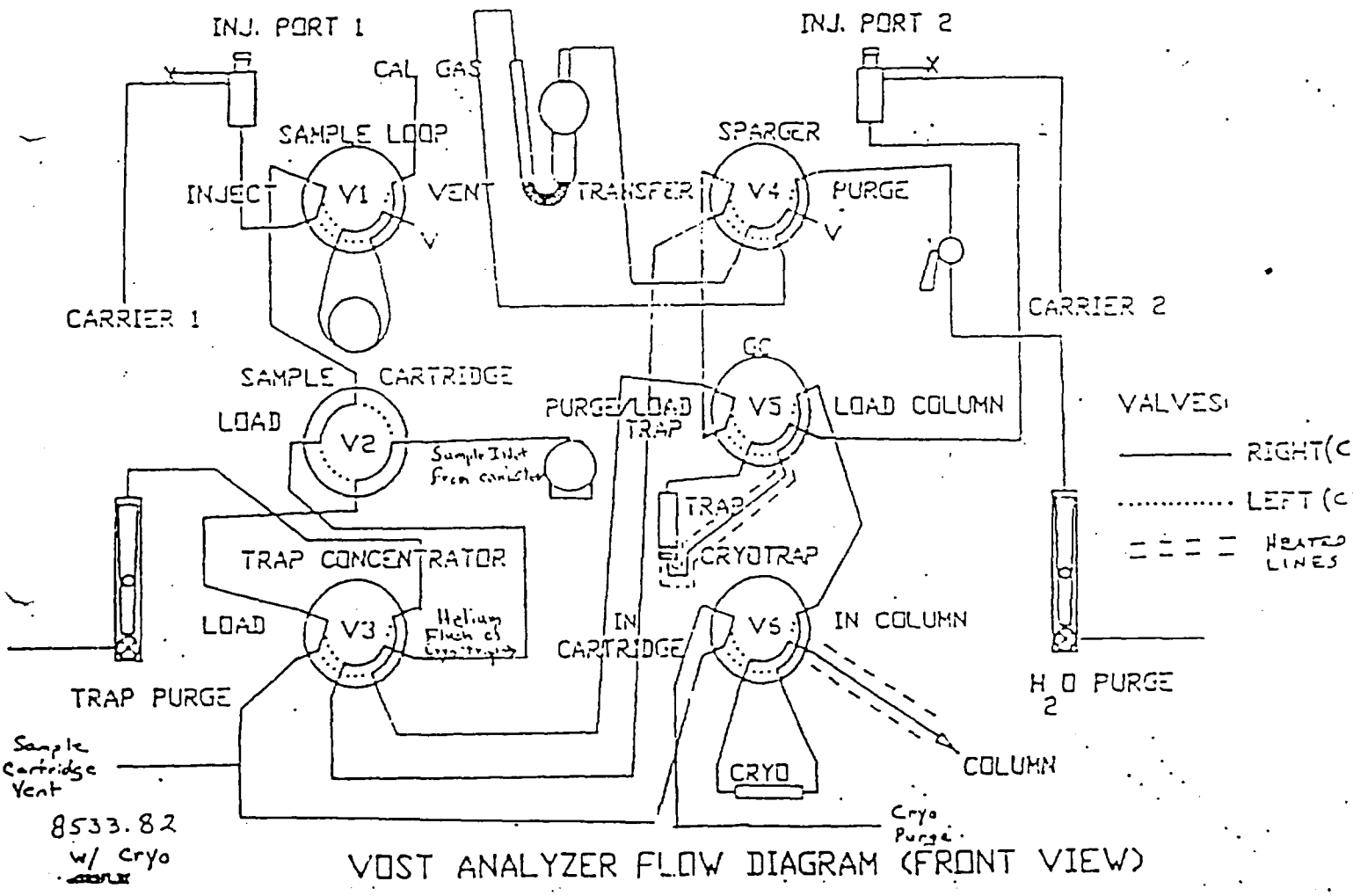

TABLE 2. Cylinder No. CC72069

Component	Concentration (v/v)
Chloromethane	0.98 ± 0.05 ppm
Bromomethane	1.00 ± 0.05 ppm
Chloroethane	0.96 ± 0.05 ppm
Dichloromethane	1.08 ± 0.05 ppm
trans-1,2-Dichloroethylene	1.08 ± 0.05 ppm
Trichloroethane	1.07 ± 0.05 ppm
1,2-Dichloroethane	1.10 ± 0.05 ppm
1,1,1-Trichloroethane	0.99 ± 0.05 ppm
Tetrachloromethane	1.01 ± 0.05 ppm
1,2-Dichloropropane	1.08 ± 0.05 ppm
cis-1,3-Dichloropropene	1.03 ± 0.05 ppm
trans-1,3-dichloropropene	1.20 ± 0.06 ppm
Dibromochloromethane	1.13 ± 0.05 ppm
Tetrachloroethylene	1.14 ± 0.05 ppm
Ethylbenzene	1.20 ± 0.06 ppm
p-Xylene	1.20 ± 0.06 ppm
Styrene	1.25 ± 0.06 ppm
1,1,2,2-Tetrachloroethane	1.24 ± 0.06 ppm
Bromodichloromethane	1.08 ± 0.05 ppm
Trichloroethene	0.82 ± 0.05 ppm
Acetonitrile	1.00 ± 0.05 ppm
Nitrogen	Balance

TABLE 3. Standard Cylinder No. CC72058

Component	Concentration (v/v)
Carbon Disulfide	4.86 ± 0.1 ppm
Nitrogen	Balance

TABLE 4. Standard Cylinder No. CC72063

Component	Concentration (v/v)
Vinyl Chloride	1.00 ± 0.05 ppm
1,1-Dichloroethene	1.08 ± 0.05 ppm
1,1-Dichloroethane	1.06 ± 0.05 ppm
2-Butanone	1.02 ± 0.05 ppm
cis-1,2-Dichloroethene	1.07 ± 0.05 ppm
Benzene	1.07 ± 0.05 ppm
4-Methyl-2-pentanone	1.09 ± 0.05 ppm
1,1,2-Trichloroethane	1.06 ± 0.05 ppm
Toluene	1.08 ± 0.05 ppm
2-Hexanone	1.18 ± 0.05 ppm
Chlorobenzene	1.08 ± 0.05 ppm
m-Xylene	1.11 ± 0.05 ppm
o-Xylene	1.12 ± 0.05 ppm
1,2-Dichlorobenzene	1.25 ± 0.05 ppm
Acetone	0.99 ± 0.05 ppm
1,4-Dichlorobenzene	1.04 ± 0.05 ppm
Nitrogen	Balance

TABLE 5. Standard Cylinder No. CC12390

Component	Concentration (v/v)
Freon-12	1.015 ± 0.05 ppm
Freon-114	0.95 ± 0.05 ppm
Freon-11	0.94 ± 0.05 ppm
Freon-113	0.99 ± 0.05 ppm
n-Hexane	1.02 ± 0.05 ppm
1,2-Dibromoethane	0.99 ± 0.05 ppm
4-Ethyltoluene	0.89 ± 0.05 ppm
1,3,5-Trimethylbenzene	0.95 ± 0.05 ppm
1,2,4-Trimethylbenzene	0.92 ± 0.05 ppm
Nitrogen	Balance

TABLE 6. Internal Standard Liquid Mix

Component	Concentration (ug/ml)
Bromochloromethane	1000
1,4-Difluorobenzene	1000
Chlorobenzene-d5	1000

TABLE 7. Standard Cylinder No. ALM 002636

Component	Concentration (v/v)
Benzyl chloride	0.737 ppm
1,3-Dichlorobenzene	0.768 ppm
1,4-Dioxane	0.895 ppm
Hexachloro-1,3-butadiene	0.804 ppm
Bromoform	0.84 ppm
1,2,4-Trichlorobenzene	0.898 ppm
Vinyl acetate	0.838 ppm
Nitrogen	

8. Procedure

8.1 Sample Preparation

8.1.1 The pressure of the sample canister is checked and recorded by attaching a vacuum/pressure gauge to the top valve of the canister (the gauge should be rinsed for few seconds with HC free air by physically holding against the air outlet and flushing). The canister valve is opened briefly and the pressure is recorded. If the pressure is less than 10 psig, pressurize the canister to 10 psig with HC free air.

8.1.2 If the canister pressure is increased, a dilution factor (DF) is calculated and recorded.

$$DF = \frac{Y_a}{X_a}$$

Where: X_a = absolute canister pressure absolute before dilution

Y_a = absolute canister pressure absolute after dilution

8.2 Daily GC/MS Tuning

8.2.1 At the beginning of each day or prior to a calibration, the GC/MS system must be tuned to verify that acceptable performance criteria are achieved. If any of the key ions fail the abundance criteria listed in Table 8, the system must be retuned using 4-Bromofluorobenzene (BFB).

8.2.2 For daily tuning, the relays on the Nutech controller (see Figure 1) should be in the right hand position, with the cryo trap at 150°C (alternatively valves 2 and 6 could be placed in the left hand position with the auxiliary He flow set at 10 ml/min or greater). The GC program is initiated by using the Datac command in file manager (FMGR). The GC program is named "GCBFB1." This downloads the program from the data system to the GC. Once the oven has stabilized, the remote start light will turn on and the system is ready for injection.

1 uL of a 50 ng/uL 4-bromofluorobenzene (BFB) standard is injected into injection port 2 of the Nutech 8533 and the remote start button is activated.

TABLE 8. 4-Bromofluorobenzene Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 96
175	5 to 9% of mass 174
176	>95% but <101% of mass 174
177	5 to 9% of mass 176

8.2.3 Once the tuning run is complete (~ 8 minutes), review a scan close to the center of the BFB peak. If it looks close to passing, type in the command TRF, TUNVOA, data file. This will start a program that will find a scan that will pass the tuning and print out the required information automatically. If the BFB tuning criteria cannot be met on 2-3 injections, retuning the instrument with PFTBA may be required.

TABLE 9. BFB Tuning Method

Enter the name of the method file: GCBFB1

M E T H O D F I L E L I S T

Method file: GCBFB1 GC type: 5890 Column: Cap Run type: SCAN, GC, EI Splitless: Yes

Temperature:	Inj.P	Intfc	Source
	90.0	250.0	0.0

GC/DIP		LEVEL A	LEVEL B	POST RUN
Temp 1	30.0	100.0	0.0	0.0
Time 1	1.0	15.0	0.0	0.0
Rate	35.0	0.0	0.0	
Temp 2	100.0	0.0	0.0	
Time 2	15.0	0.0	0.0	

Oven equilibration Time .10 min

Run time: 6.00
Scan Start time: 2.50
Splitless valve time: .80

	ON	OFF	ON	OFF
Relay #1:	327.0	327.0	327.0	327.0
Relay #2:	327.0	327.0	327.0	327.0
Triac #0:	327.0	327.0	327.0	.0
Triac #1:	327.0	327.0	327.0	327.0

Scan Parameters: Mass Range 35 to 260
Multiplier voltage: 2244 Number of A/D samples: 8
GC Peak threshold: 20000 counts
Threshold: 100 counts

TABLE 10. Analytical Method

Enter the name of the method file: GCTO14

M E T H O D F I L E L I S T

Method file: GCTO14 | GC type: 5890 | Column: Cap | Run type: SCAN, GC, EI | Splitless: Yes

Temperature:	Inj.P	Intfc	Source
	90.0	250.0	0.0

GC/DIP		LEVEL A	LEVEL B	POST RUN
Temp 1	-50.0	-20.0	127.0	0.0
Time 1	2.0	0.0	20.0	0.0
Rate	70.0	5.0	0.0	
Temp 2	-20.0	127.0	0.0	
Time 2	0.0	20.0	0.0	

Oven equilibration Time .10 min

Run time: 32.10
Scan Start time: .10
Splitless valve time: 0.00

	ON	OFF	ON	OFF
Relay #1:	327.0	327.0	327.0	327.0
Relay #2:	327.0	327.0	327.0	327.0
Triac #0:	327.0	327.0	327.0	327.0
Triac #1:	327.0	327.0	327.0	327.0

Scan Parameters: Mass Range 35 to 260
Multiplier voltage: 2244 Number of A/D samples: 8
GC Peak threshold: 20000 counts
Threshold: 10 counts

8.3 Calibration

8.3.1 A static dilution of the stock standard gas mixtures is made in a 6 liter canister. The high precision vacuum gauge is flushed with HC free air and attached to the top valve of a clean, evacuated canister. After recording the absolute pressure, 2 psi of each of the 5 standard mixtures is added to the canister (each regulator and the transfer line must be

flushed several times before transfer of standard to the canister). Close the canister valves and replace the high precision gauge with a vacuum/pressure gauge. Pressurize the can with HC free air to 30 psig. This will yield a standard with a nominal concentration of 44 ppbv for most compounds (see Table 11).

8.3.2 An initial 5 point curve is run in the linear working range of the system. The nominal concentration of the 5 standards will be 18 ppbv, 67 ppbv, 90 ppbv, 224 ppbv and 287 ppbv.

8.3.3 On a daily basis, a one point midrange standard (500 ml of 44 ppbv) is run to verify the 5 point curve. 90% of the target compounds must be within 30% of the 5 point curve, or a new 5 point must be run. The daily, one point check standard is used to calculate the concentration of the samples.

8.3.4 After the calibration runs and the QA/QC sample runs, an HC free air blank is run. This must be < the MDL for each target compound.

8.4 Analysis

8.4.1 The daily check standard and the QA/QC samples are analyzed the same as samples. The HC free air blank is a system blank and differs only in that it is not transferred to a canister, but run directly from the cylinder regulator to the sample inlet system.

8.4.2 The sample canister is connected to the sample inlet system. The Nutech controller should have valves 2 and 6 in the left hand position, while valves 1 and 3-5 should be in the right hand position. The auxiliary He flow should be set at 40 ml/minute. The canister valve is opened and the pressurized sample is allowed to flow through the mass flow controller (set at 50 ml/min) and out the vent line.

8.4.3 The cryogenic trap is cooled to its lower set point of -170°C. When the cryo trap reaches -170°C, the Nutech valve #2 is switched to the right hand position and a timer is started. After 10 minutes (500 mL) valve #2 is switched back to the left hand position. Thus 500 ml of blank, standard or sample is concentrated on the cryo trap.

8.4.4 The valve on the sample canister is closed and the remaining line pressure is allowed to drop to ambient. The 3-way valve is then switched to the internal standard canister and the I.S. canister valve is opened and allowed to flush for at least 2 minutes. (The internal standard is made by injecting 20 ul of the liquid mix int an evacuated canister and pressurizing to 30 psi(44.6 psia). Valve is then switched to the right hand position and a timer is started After 2 minutes, Valve 2 is switched back to the left hand positio Thus 100 ml of 200 ppbv nominal internal standard mix is injected the cryotrap with each blank, standard or sample.

8.4.5 The GC is cooled to its' initial set point of -50°C by using Datac in file manager. The name of the GC program is "GCTO14." This takes about 2.5 minutes. During this time valves 2 and 6 remain in the left hand position, allowing He to sweep the trap and remove most oxygen, nitrogen and other permanent gases.

8.4.6 When the GC has reached equilibrium the red remote start light will turn on. Switch valve #6 to the right hand position. Wait at least 10 seconds to allow flow through the trap to equilibrate. The blue "cool" button on the Nutech controller and remote start button should be pressed simultaneously. This will heat the cryo trap to 150°C and start the GC program.

9. Data Interpretation

9.1 Qualitative Analyses

9.1.1. An analyte (e.g., those listed in Table 1) is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained on the user's GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification. (1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

9.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hours as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

9.1.1.2 (1) All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum. (2) The relative intensities of ions specified in (1) must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the correspondin sample abundance must be must be between 30 and 70 percent.

9.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

9.2 Quantitative Analysis:

When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary charateristic ion. Quantification will take place using the internal standard technique.

10. QA/QC Requirements

10.1 The mass spectrometer must meet the tuning criteria described in Section 8.2.

10.2 After tuning, a single point check standard must be analyzed. Ninety percent of the target compound concentrations must be within ± 30% of the ~~three~~ five point calibration curve. If the check standard fails to meet this criterion, a new ~~three~~ five point calibration curve must be run.

PL 6/5/90

10.3 A laboratory control sample (LCS) must be analyzed after the check standard. This sample will consist of the target VOCs prepared in a separate canister at a concentration that differs from that of the check standard. Five compounds will be used to assess control for the LCS: methylene chloride, 1,1-dichloroethene, trichloroethene, toluene and 1,1,2,2-tetrachloroethane. The percent recovery for the five control compounds must be within a window of 80-115%.

10.4 For each lot of 20 samples analyzed, a duplicate control sample (DCS) must be analyzed after the LCS. The DCS sample is identical to the LCS in composition and source. The 80-115% recovery criterion must be met. In addition, the relative percent difference (RPD) for the LCS and DCS must be ≤ 20%.

10.5 A system blank of HC free air must be analyzed after the LCS or DCS. The blank results must indicate that there are no target compounds present above the MDL.

10.6 If any of the above criteria are not met, corrective actions must be implemented before analyses can proceed.

11. Calculations

11.1 The HP data system automatically quantitates the sample results based on a 500 mL sample size. The results are in ppbv. If the canister was pressurized before analysis, the results must be multiplied by the dilution factor DF (see Section 8.1.2).

11.2 If a sample size other than 500 mL was used, the result must be adjusted as shown below:

$$\text{result ppbv} \times \frac{\text{sample volume injected}}{500 \text{ mL}}$$

12. Reporting

12.1 Reporting units are ppbv. If results are to be reported in ng/L use the following equation:

$$\text{result ppbv} \times \frac{\text{Molecular weight of compound}}{24.5} = \text{ng/L}$$

Note: 24.5 is the standard volume of ideal gas at 25 degrees Centigrade and 1 atm.

12.2 Reporting limits

See Table 12

12.3 Significant figures

12.3.1 All results should be reported to two significant figures.

12.3.2 Only report results below detection limit as ND(DL).

12.4 No conversion of the analytical results to the standard conditions is made.

13. References

13.1 Method Source

"EPA Compendium Method TO-14. The Determination of Volatile Organic Compounds (VOCs) in Ambient Air using SUMMA Passivated Canister Sampling and Gas Chromatographic Analysis."

13.2 Deviations from Method

13.2.1 Dry HC free air is used for the daily blank and for dilution purposes.

13.2.2 TO-14 recommends the use of a .32 mm column coupled directly to the MSD. With the HP system, the MSD can only handle flow of 1 mL/min or less. The .32 mm column provides ~ 3 mL/min. Enseco uses a .53 mm column through a jet separator.

13.2.3 TO-14 describes an inlet system that uses a vacuum to pull a slip stream sample through the trap. Enseco uses the pressure of the sample canister to drive the sample through the trap.

TABLE 11. Concentration of Daily Check Standard

	Compound	Concentration (ppbv)
42)	1,2-(ortho) Xylene	50.12
43)	Styrene	55.92
44)	Bromoform	37.58
45)	1,1,2,2-Tetrachloroethane	55.48
46)	Benzyl chloride	32.98
47)	4-Ethyltoluene	39.82
48)	1,3,5-Trimethylbenzene	42.50
49)	1,2,4-Trimethylbenzene	41.16
50)	1,3-Dichlorobenzene	34.36
51)	1,4-Dichlorobenzene	46.54
52)	1,2-Dichlorobenzene	55.92
53)	1,2,4-Trichlorobenzene	40.18
54)	Hexachlorobutadiene	35.98

Table 12. VOC Reporting Limits

	Compound	Reporting Limits (ppbv)
2)	Dichlorodifluoromethane (Freon 12)	2.0
3)	Chloromethane	2.5
4)	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	2.0
5)	Vinyl chloride	2.5
6)	Bromoethane	3.0
7)	Chloroethane	5.0
8)	Trichlorofluoromethane (11)	1.0
9)	cis-1,2-Dichloroethene	2.0
10)	Carbon disulfide	10
11)	1,1,2-Trichloro- 1,2,2-trifluoroethane (Freon 113)	2.0
12)	Acetone	10
14)	Methylene chloride	4.0
15)	trans-1,2-Dichloroethene	4.0
16)	Hexane	8.0
17)	1,1-Dichloroethane	2.5
18)	Vinyl Acetate	2.5
19)	1,1-Dichloroethene	2.0
20)	2-Butanone	3.0
21)	Chloroform	2.0
22)	1,1,1-Trichloroethane	2.0
23)	Carbon tetrachloride	2.0
24)	Benzene	3.0
25)	1,2-Dichloroethane	2.0
26)	Trichloroethene	2.5
27)	1,2-Dichloropropane	8.0
28)	1,4-Dioxane	7.0
29)	Bromodichloromethane	2.0
30)	cis-1,3-Dichloropropene	3.0
31)	4-Methyl-2-pentanone	3.0
32)	Toluene	3.0
33)	trans-1,3-Dichloropropene	3.0
34)	1,1,2-Trichloroethane	3.0
35)	Tetrachloroethene	3.0
36)	2-Hexanone	5.0
37)	Dibromochloromethane	3.0
38)	1,2-Dibromoethane	2.0
39)	Chlorobenzene	2.5
40)	Ethylbenzene	2.5
41)	1,4-and 1,3-(p,m) Xylene	5.0

Table 12. VOC Reporting Limits

	Compound	Reporting Limits (ppbv)
42)	1,2-(ortho) Xylene	2.0
43)	Styrene	7.0
44)	Bromoform	2.0
45)	1,1,2,2-Tetrachloroethane	4.0
46)	Benzyl chloride	2.0
47)	4-Ethyltoluene	4.0
48)	1,3,5-Trimethylbenzene	2.5
49)	1,2,4-Trimethylbenzene	3.0
50)	1,3-Dichlorobenzene	3.0
51)	1,4-Dichlorobenzene	4.0
52)	1,2-Dichlorobenzene	5.0
53)	1,2,4-Trichlorobenzene	7.0
54)	Hexachlorobutadiene	5.0

APPENDIX B-13

CLAY MINERALOGY BY X-RAY DIFFRACTION (CORE)

4.2.2 X-ray Diffraction Standard Operating Procedures

INTRODUCTION

Parameter to be measured

The parameter to be measured in an X-ray diffraction analysis is accurate mineral content of a selected sample in weight percent.

Range of measurement

Core Laboratories uses a Philips Electronic Instruments Model 3600 Automated Powder Diffractometer. The sample holder of a Philips goniometer is connected to a center shaft, called the "Theta Shaft" and rotates at a prescribed rate which is propelled by a computer-controlled stepper motor. Each angular increment is described as theta angle increment. The detector arm is coupled to the theta shaft in a 2 to 1 fashion. All measurements of a sample are expressed as "two-theta" measurements. The Philips goniometer has a working distance of 2 degrees two-theta to 140 degrees two-theta.

The scope of phases measured includes those that are crystalline or quasi-crystalline (certain clay minerals). Amorphous materials cannot be directly measured by X-ray diffraction. Two basic groups of phases, or minerals, are considered, namely rock-forming minerals (quartz, feldspars, carbonates, sulfides, etc.) and phyllosilicates (clay minerals). The diffraction peaks of these minerals are measured and stored for later analysis.
Certain procedures are available for detection and semi-quantitative analysis of amorphous phases; however, they are currently not implemented by Core Laboratories. X-ray diffraction techniques cannot supply any qualitative information about amorphous phases unless elemental data is supplied or prior knowledge of the phase leaves no doubt to its chemical composition.

Limit of Detection

The limit of detection of X-ray diffraction of a normally prepared sample is 1 weight percent of the fraction analyzed. Various methods for concentrating certain target groups of minerals are implemented by Core Laboratories, as necessary. Also, certain conditions within the diffractograms (overlaps of two phases' diffraction peaks) may raise the detection limit of a phase. Accuracy of the diffraction analysis is $\pm$ 5 weight percent.

Principle, Scope, and Application

X-ray diffraction analysis is a method used for determining the mineral content of a substance. Most materials consist of tiny crystals which are made of ordered arrays of atoms arranged in a periodic or repetitive way. When an incident X-ray beam impinges upon such an array, general scattering occurs, such that the scattered waves interfere with and destroy one another. In certain specific directions, however, the scattered waves are in phase with one another and combine to form new wave-fronts. This constructive interference is know as diffraction. The direction in which diffraction occurs depend upon the size and shape of the unit cell of the crystal, whereas the intensity of diffraction is determined

by the actual atomic array or the nature of the crystal structure. The condition for reflection of X-rays from a parallel arrangement of atoms within a crystal is called the Bragg Angle. Bragg's Law,

$$n\ 1 = 2d\sin\ 0,$$

where, n is the order of reflection, lambda is the wavelength of incident X-rays, d is the interplanar spacing between rows of atoms and theta is the angle of the incident X-rays. This is the basic principle behind X-ray diffraction. This principle applies to crystalline materials and does not apply on amorphous substances (glass, certain organics, certain clays, etc.). For a more detailed discussion, please refer to Cullity (1967).

Each crystalline substance, or phase, has a unique set of integral peaks that are like individual fingerprints of humans. For each diffractogram, these peaks are measured in the angular expression of two-theta space, identified and indexed for future reference. A very large database (> 100,000) of phases has been compiled by the Joint Committee of Powder Diffraction Standards (JCPDS) and is available in book form and magnetic media for computer-aided search and match algorithms and for comparison to the indexed pattern for identification of phases in the diffractogram. The intensity of a diffraction peak of a phase is indirectly proportional to the concentration of the phase. There are a number of phenomenon that need to be considered when doing a quantitative analysis on multiphase substances. Please refer Klug and L. E. Alexander for more detail on this matter.

SAMPLE PREP AND ANALYSIS

Sample Requirements

Sample supplied for X-ray diffraction must be a representative portion of the sample. Approximately 10 grams are required for a routine analysis. No preservation is necessary other than insuring the sample was maintained at ambient conditions after coring.

Sample Preparation

Sample selected for X-ray diffraction analysis is dried and cleaned of obvious contaminants. For hydrocarbon removal, the sample is placed in a low temperature, methylene chloride soxhlet for 24 hours. The sample is gently ground in a ceramic mortar and pestle and split into two equal portions using a riffle splitter. One split is saved for later milling for a bulk analysis pellet. This procedure is described later. The remaining split is tested for halides (silver nitrate test). If needed, the sample is placed in a low-temperature methanol soxhlet for up to 72 hours, or until sample is leached of all halides. The sample is weighed and placed in 150 milliliters of deionized water treated with 1 volume percent Calgon water softener and treated with a sonic cell disrupter for 5 minutes. This procedure breaks the clay from host grains and breaks down lithic fragments containing clay. The Calgon is added to aid in clay dispersion. The resultant slurry is placed in a

centrifuge in order to fractionate the sample at 2 microns. The suspended < 2 micron fraction is decanted and saved, and the > 2 micron fraction is washed and centrifuged again to remove any < 2 micron particles. The remaining < 2 micron particles are added to the saved < 2 micron portion. The > 2 micron fraction is dried and weighed to determine the percent of clay- and silt-sized material. This weight is used to determine the net clay of the sample. The suspended < 2 micron fraction is suctioned onto a pure silver substrate with an average pore diameter of 1.2 microns. The resulting aggregate of sample and substrate is dried and mounted on a glass slide. The > 2 micron fraction and the previously saved split of sample are milled in a McCrone micronizing mill with low-water isopropanol and then packed into sample holders for analysis. The > 2 micron fraction and the bulk split are scanned from 2 to 60 degrees two-theta at 1 degree per minute. The < 2 micron sample mount is run first in the natural (air-dried) state and then treated with ethylene glycol vapor for 24 hours and run again. Both clay runs are from 2 to 40 degrees at 1 degree per minute.

Apparatus

The sample is analyzed with a Philips APD 3600 X-ray diffractometer at a slow rate (1 degree/minute) using a copper tube (wavelength CuK alpha$_1$ = 1.54051 angstroms) with 35 kilovolt potential and 35 milliamp current. Scintillator voltage is 800 volts and time constant is 1. A Data General Nova 4X is used to the collect and store data while a Data General Eclipse S/140 is used for data reduction.

Analytical Measurements

The diffractograms for each run are first inspected for any data collection anomalies and the samples are scanned again if necessary. The bulk split is analyzed for any water-soluble minerals. The bulk split is also compared to the > 2 micron sample for consistency, clays, et cetera. If any inconsistencies are identified, the sample may be rerun. If any water-soluble minerals are detected, they are quantified and added to the total mineral analysis.

Minerals in the >2 micron powder mount and clay mount are identified by comparison of the diffractograms to standards, either prepared and run on Philips diffractometer or standards from the Joint Committee on Powder Diffraction Standards. A computer algorithm is available for complex pattern or for rare mineral phases which matches the unknown pattern to those of the JCPDS for accurate phase identification. Most of the clay mineral standards are patterns that were run on the Philips diffractometer. Certain clay minerals called "mixed-layer clays" are found in many sediments. Occasionally, it is not possible to collect standards for every mixed-layer clay that could be anticipated in a given basin. Therefore, Core Laboratories uses a computer algorithm developed by Reynolds that calculates a pattern of mixed-layer clay based on unit cell and chemical formulae restrictions. The resulting calculated pattern intensities are analyzed with the profile-fitting algorithm and then intensity relationships are

established. Compositions and species of the clay minerals are determined according to procedures outlined by Reynolds (1980, 1985), Grim (1962), Wilson (1987), Srodon (1980, 1984), Carroll (1970).

The integrated areas of the most intense reflection for each phase are obtained using a multiple Lorentzian profile-fitting algorithm (Schreiner and Jenkins, 1983) which is part of an analytical software package provided with the Philips diffractometer. Some modifications were made by Core Laboratories to the source code of the profile-fitting algorithm to make it more efficient. The integrated areas are corrected for various absorption and orientation phenomena with structure factors obtained from previous calibrations of each phase using a modified Chung method (1974a, b, and c). The corrected integrated areas are normalized to 100 percent. Any clay minerals trapped in the > 2 micron fraction are quantified and mathematically added to the clay category. Any rock-forming minerals trapped in the < 2 fraction are also mathematically removed and added to the rock-forming mineral category. The integrated area for each phase is entered into a spreadsheet that calculates the weight percent data. The results are then tabulated and sorted according to depth or any relevant sample identification.

Interferences and corrective actions

Particle size plays an important part of the diffraction intensity. Too small a particle size produces a small and broad diffraction peak, and in extreme cases, the peak of phase with too small a particle size can no longer diffract X-rays and completely disappear due to extensive lattice damage. Too large a particle size produces primary extinction effects and also can lead to preferred orientation. A completely random ordering of crystallites in a powder mount is most preferred because preferred cleavage planes are often the most intense diffraction planes which could lead to overestimation of the orienting phase. Conversely, clay minerals are often oriented by using a suction or settling method because they are not as efficient as diffracting X-rays along what are called their "hkl" planes. Clay minerals are typically flat, platey crystals with the edge surfaces being the hkl planes of the clay mineral crystallites. Basal planes of clay minerals are aligned with the long axis of the crystallite, consequently when the clay crystallite is aligned along the long axis, it diffracts much more efficiently due to an ideal arrangement of atoms along the basal or "001" plane and integrals.

Salts are a problem with respect to water separating the sample to < 2 and > 2 microns because as the halite goes into solution it provides a nucleating site for the strongly negatively charged clay particles. As the clays nucleate, or flocculate, onto cations in solution, the clays tend to fall out of suspension immediately, thus ruining the gravimetric portion of the experiment. That is why the salts are removed with methanol if their presence is detected. It does not take very much salt to ruin the procedure.

Hydrocarbons are also a problem with respect to preparation of samples because they tend to cause the sand to ball up and float on the surface. Consequently, if detected or suspected, the soluble hydrocarbons are removed with methylene chloride. Any insoluble hydrocarbons remain behind but cause no major sample prep problems.

A large source of error in diffraction is the overlap of two or more peaks at the same or proximal two-theta positions. This is minimized by performing profile-fitting (not deconvolution) of overlapped areas of the diffractograms. One particularly notorious overlap is that between two clay minerals, kaolinite and chlorite. If these two minerals (one occurring at 24.9 and 25.2 degrees two theta, respectively) were quantified by peak intensity only, errors as high as 100% may occur.

The silver substrate below the deposited clay minerals often is detected in a diffractogram as elemental silver. This is due to the finite thickness of the clay on the silver substrate. If not accounted for, errors will be generated by comparing intensities from low two theta angles to intensities from high two theta angles. The error occurs due to the path distance differential of the incident X-ray beam. At low two-thetas, the path distance will be much larger due to the larger incident angle, consequently giving a much larger intensity of a diffraction peak than that of a diffraction peak from a higher two-theta. At higher two-thetas, the path distance is much shorted due to the higher incident angle. This must be corrected by applying the formula

$$I_{inf} = I_{thin}/[1-\exp(-2ut/\sin\ 0)]$$

that corrects all two-theta position intensities to those of an infinitely thick mount. By measuring the intensity of the silver peak on the unknown sample versus that of an external standard of pure silver, the exact thickness of the sample substrate can be calculated and all intensities can be converted to that of infinitely thick "powder mount".

Poor alignment of the X-ray diffractometer can also lead to serious errors and is remedied by frequently observing the most intense peak (101 - hkl index) of alpha quartz which occurs at approximately 26.66 degrees two theta and making adjustments to goniometer position as needed. Any time a diffractometer is moved, it is necessary to do a "ground up" alignment.

Calibration

Calibration of the rock-forming minerals was accomplished by running a series of external standard mineral phases, tested for purity and known for their abundance of source, against alpha quartz as a flushing agent (Chung, 1974). Ten mixtures of each phase with quartz, in graduated amounts from 0 to 100 percent, were analyzed and the ratio of observed versus actual concentrations were plotted. A non-weighted, least-squares regression analysis was performed on each data set to evaluate the best fit line

through the data. The slope and y-intercept of each phase were used to calculate a normalized intensity correction coefficient for each standard. This correction coefficient is free of matrix absorption effects and is also free of orientation effects since the standards and the unknowns are prepared in the same fashion. The clay minerals were calibrated in a similar fashion with the exception of chlorite (CCa-1, ripidolite) replacing quartz. This was repeated for each phase. Up to 70 minerals have now been calibrated.

Data Deliverables

As requested, the following will be provided

a) Case narrative as outlined.

b) Summary of initial calibration as detailed above. This calibration is performed only once until a major change is effected.

c) Summary of sample analysis as outlined.

d) QC analyses are not routinely performed. Can be effected upon request.

e) Diffractograms will be provided.

f) Instrument logbook will be provided as requested.

Safety Precautions

Core Laboratories is fully licenced facility registered with the Texas Department of Health for operating radiation generating devices. A site survey was performed in August, 1990 by Henken Industries for site leakage of X-rays and were deemed operating at a safe (minimal) exposure level. All employees wear both deep and shallow dose radiation detection devices that are monitored on a monthly basis. All employees are sufficiently trained in the safe operation of the X-ray diffractometer and appropriate warnings and advisements are posted in proximity to the machine and at all doors entering into the laboratory.

Our laboratory staff practice all safety procedures for handling hazardous materials and wear all accoutrements necessary for safe laboratory operation.

Preventative Maintenance

No preventative maintenance is required for the X-ray diffractometer other than checking cooling water levels in the heat exchanger and checking the overall appearance and insuring that all safety interlocks are functioning properly.

Quality Control

Besides data quality checks by the X-ray analyst, quality control as a strict regimen is not observed; however numerous cross checks are performed when thin section or FTIR analyses are performed.

Any discrepancies observed are promptly investigated and, if necessary, samples are re-analyzed to check results.

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APPENDIX B-14

NATURAL MOISTURE CONTENT (WARZYN)

Designation: D 2216 – 80

An American National Standard

Standard Method for LABORATORY DETERMINATION OF WATER (MOISTURE) CONTENT OF SOIL, ROCK, AND SOIL-AGGREGATE MIXTURES[1]

This standard is issued under the fixed designation D 2216; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This method covers the laboratory determination of the water (moisture) content of soil, rock, and soil-aggregate mixtures by weight. For simplicity, the word "material" hereinafter refers to either soil, rock, or soil-aggregate mixtures, whichever is most applicable.

1.2 The water content of a material is defined as the ratio, expressed as a percentage, of the mass of "pore" or "free" water in a given mass of material to the mass of the solid material particles.

1.3 This method does not give true representative results for: materials containing significant amounts of halloysite, montmorillonite, or gypsum minerals; highly organic soils; or, materials in which the pore water contains dissolved solids (such as salt in the case of marine deposits). For a material of the previously mentioned types, a modified method of testing or data calculation may be established to give results consistent with the purpose of the test.

2. Summary of Method

2.1 The practical application in determining the water content of a material is to determine the mass of water removed by drying the moist material (test specimen) to a constant mass in a drying oven controlled at 110 ± 5°C and to use this value as the mass of water in the test specimen. The mass of material remaining after oven-drying is used as the mass of the solid particles.

3. Significance and Use

3.1 For many soil types, the water content is one of the most significant index properties used in establishing a correlation between soil behavior and an index property.

3.2 The water content of a soil is used in almost every equation expressing the phase relationships of air, water, and solids in a given volume of material.

3.3 In fine-grained (cohesive) soils, the consistency of a given soil type depends on its water content. The water content of a soil, along with its liquid and plastic limit, is used to express its relative consistency or liquidity index.

3.4 The term "water" as used in geotechnical engineering, is typically assumed to be "pore" or "free" water and not that which is hydrated to the mineral surfaces. Therefore, the water content of materials containing significant amounts of hydrated water at in-situ temperatures or less than 110°C can be misleading.

3.5 The term "solid particles" as used in geotechnical engineering, is typically assumed to mean naturally occurring mineral particles that are not readily soluble in water. Therefore, the water content of materials containing extraneous matter (such as cement, etc), water-soluble matter (such as salt) and highly organic

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[1] *This method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity and Density Characteristics of Soils.*

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matter typically require special treatment or a qualified definition of water content.

4. Apparatus

4.1 *Drying Oven*, thermostatically-controlled, preferably of the forced-draft type, and maintaining a uniform temperature of 110 ± 5°C throughout the drying chamber.

4.2 *Balances*, having a precision (repeatability) of ±0.01 g for specimens having a mass of 200 g or less, ±0.1 g for specimens having a mass of between 200 and 1000 g, or ± 1 g for specimens having a mass greater than 1000 g.

4.3 *Specimen Containers*—Suitable containers made of material resistant to corrosion and a change in mass upon repeated heating, cooling, and cleaning. Containers with close-fitting lids shall be used for testing specimens having a mass of less than about 200 g; while for specimens having a mass greater than about 200 g, containers without lids may be used (Note 1). One container is needed for each water content determination.

NOTE 1—The purpose of close-fitting lids is to prevent loss of moisture from specimens before initial weighing and to prevent absorption of moisture from the atmosphere following drying and before final weighing.

4.4 *Desiccator*—A desiccator of suitable size (a convenient size is 200 to 250-mm diameter) containing a hydrous silica gel. This equipment is only recommended for use when containers having close-fitting lids are not used. See 7.4.1.

5. Samples

5.1 Keep the samples that are stored prior to testing in noncorrodible airtight containers at a temperature between approximately 3 and 30°C and in an area that prevents direct contact with sunlight.

5.2 The water content determination should be done as soon as practicable after sampling, especially if potentially corrodible containers (such as steel thin-walled tubes, paint cans, etc.) or sample bags are used.

6. Test Specimen

6.1 For water contents being determined in conjunction with another ASTM method, the method of specimen selection specified in that method controls.

6.2 The manner in which the test specimen is selected and its required mass is basically dependent on the purpose (application) of the test, type of material being tested, and the type of sample (specimen from another test, bag, tube, split-barrel, etc.). In all cases, however, a representative portion of the total sample shall be selected. If a layered soil or more than one soil type is encountered, select an average portion or individual portions or both, and note which portion(s) was tested in the report of the results.

6.2.1 For bulk samples, select the test specimen from the material after it has been thoroughly mixed. The mass of moist material selected shall be in accordance with the following table:

Sieve Retaining More Than About 10 % of Sample	Recommended Minimum Mass of Moist Specimen, g
2.0 mm (No. 10) sieve	100 to 200
4.75 mm (No. 4) sieve	300 to 500
19 mm	500 to 1000
38 mm	1500 to 3000
76 mm	5000 to 10 000

6.2.2 For small (jar) samples, select a representative portion in accordance with the following procedure:

6.2.2.1 For cohesionless soils, thoroughly mix the material, then select a test specimen having a mass of moist material in accordance with the table in 6.2.1. See Note 2.

6.2.2.2 For cohesive soils, remove about 3 mm of material from the exposed periphery of the sample and slice it in half (to check if the material is layered) prior to selecting the test specimen. If the soil is layered see 6.2. The mass of moist material selected should not be less than 25 g or should be in accordance with the table in 6.2.1 if coarse-grained particles are noted. (Note 2).

6.3 Using a test specimen smaller than the minimum mass indicated previously requires discretion, though it may be adequate for the purpose of the test. A specimen having a mass less than the previously indicated value shall be noted in the report of the results.

NOTE 2—In many cases, when working with a small sample containing a relatively large coarse-grained particle, it is appropriate not to include this particle in the test specimen. If this occurs, it should be noted in the report of the results.

7. Procedure

7.1 Select representative test specimens in accordance with Section 6.

7.2 Place the moist specimen in a clean, dry container of known mass (Note 3), set the lid securely in position, and determine the mass of the container and moist material using an appropriate balance (4.2). Record these values.

7.3 Remove the lid and place the container with moist material in a drying oven maintained at 110 ± 5°C and dry to a constant mass (Notes 4, 5, and 6).

NOTE 3—To assist in the oven-drying of large test specimens, they should be placed in containers having a large surface area (such as pans) and the material broken up into smaller aggregations.

NOTE 4—The time required to obtain constant mass will vary depending on the type of material, size of specimen, oven type and capacity, and other factors. The influence of these factors generally can be established by good judgment, and experience with the materials being tested and the apparatus being used. In most cases, drying a test specimen over night (about 16 h) is sufficient. In cases where there is doubt concerning the adequacy of drying, drying should be continued until the mass after two successive periods (greater than ½ h) of drying indicate an insignificant change (less than about 0.1 %). Specimens of sand may often be dried to constant mass in a period of about 4 h, when a forced-draft oven is used.

NOTE 5—Oven-drying at 110 ± 5°C does not always result in water content values related to the intended use or the basic definition especially for materials containing gypsum or other minerals having significant amounts of hydrated water or for soil containing a significant amount of organic material. In many cases, and depending on the intended use for these types of materials, it might be more applicable to maintain the drying oven at 60 ± 5°C or use a vacuum desiccator at a vacuum of approximately 133 Pa (10 mm Hg) and at a temperature ranging between 23 and 60°C for drying. If either of these drying methods are used, it should be noted in the report of the results.

NOTE 6—Since some dry materials may absorb moisture from moist specimens, dried specimens should be removed before placing moist specimens in the oven. However, this requirement is not applicable if the previously dried specimens will remain in the drying oven for an additional time period of about 16 h.

7.4 After the material has dried to constant mass remove the container from the oven and replace the lid. Allow the material and container to cool to room temperature or until the container can be handled comfortably with bare hands and the operation of the balance will not be affected by convection currents. Determine the mass of the container and oven-dried material using the same balance as used in 7.2. Record this value.

7.4.1 If the container does not have a lid, weigh the container and material right after their temperatures are such that the operation of the balance will not be affected by convection currents or after cooling in a desiccator.

NOTE 7—Cooling in a desiccator is recommended since it prevents absorption of moisture from the atmosphere during cooling.

8. Calculation

8.1 Calculate the water content of the material as follows:

$$w = [(W_1 - W_2)/(W_2 - W_c)] \times 100 = \frac{W_w}{W_s} \times 100$$

where:

w = water content, %,
W_1 = mass of container and moist specimen, g,
W_2 = mass of container and oven-dried specimen, g,
W_c = mass of container, g,
W_w = mass of water, g, and
W_s = mass of solid particles, g.

9. Report

9.1 The report (data sheet) shall include the following:

9.1.1 Identification of the sample (material) being tested, by boring number, sample number, test number, etc.

9.1.2 Water content of the specimen to the nearest 0.1 % or 1 %, depending on the purpose of the test.

9.1.3 Indication of test specimen having a mass less than the minimum indicated in Section 6.

9.1.4 Indication of test specimen containing more than one soil type (layered, etc).

9.1.5 Indication of the method of drying if different from oven-drying at 110 ± 5°C.

9.1.6 Indication of any material (size and amount) excluded from the test specimen.

10. Precision and Accuracy

10.1 Requirements for the precision and accuracy of this test method have not yet been developed.

Y _____ DATE _____ JOB NAME _____ JOB NO. _____

CHECKED BY _____ _____ SHEET _____ OF _____

SAMPLE NO.										
MATERIAL.										
UNCONFINED COMP.										
DIA, in.										
INITIAL HT, in.										
FINAL HT, in.										
MAX LOAD, lbs.										
Qa, tsf.										
Qu, tsf.										
UNIT WEIGHT										
DIA, in.										
LENGTH, in.										
WEIGHT, gms.										
~ NM										
DRY UNIT WEIGHT pcf.										
NATURAL MOIST.										
CAN NO.										
WET WT, gms.										
DRY WT, gms.										
TARE, gms.										
% MOISTURE.										
LIQUID LIMIT										
CAN NO.										
WET WT, gms.										
WT, gms.										
TARE, gms.										
BLOW MULT										
% MOISTURE.										
PLASTIC LIMIT										
CAN NO.										
WET WT, gms.										
DRY WT, gms.										
TARE. gms.										
% MOISTURE										
ORGANIC										
CUP NO.										
START WT, gms.										
END WT, gms.										
TARE, gms.										
% LOSS.										

REMARKS:

APPENDIX B-15

ATTERBERG LIMITS (WARZYN)

Designation: D 4318 – 84

Standard Test Method for LIQUID LIMIT, PLASTIC LIMIT, AND PLASTICITY INDEX OF SOILS[1]

This standard is issued under the fixed designation D 4318; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This test method has been approved for use by agencies of the Department of Defense and for listing in the DoD Index of Specifications and Standards.

1. Scope

1.1 This test method covers the determination of the liquid limit, plastic limit, and the plasticity index of soils as defined in Section 3.

1.1.1 Two procedures for preparing test specimens and two procedures for performing the liquid limit are provided as follows:

A Multipoint test using a wet preparation procedure, described in Sections 10.1, 11, and 12.

B Multipoint test using a dry preparation procedure, described in Sections 10.2, 11, and 12.

C One-point test using a wet preparation procedure, described in Sections 13, 14, and 15.

D One-point test using a dry preparation procedure, described in Sections 13, 14, and 15.

The procedure to be used shall be specified by the requesting authority. If no procedure is specified, Procedure A shall be used.

NOTE 1—Prior to the adoption of this test method, a curved grooving tool was specified as part of the apparatus for performing the liquid limit test. The curved tool is not considered to be as accurate as the flat tool described in 6.2 since it does not control the depth of the soil in the liquid limit cup. However, there are some data which indicate that typically the liquid limit is slightly increased when the flat tool is used instead of the curved tool.

1.1.2 The plastic limit test procedure is described in Sections 16, 17, and 18. The plastic limit test is performed on material prepared for the liquid limit test. In effect, there are two procedures for preparing test specimens for the plastic limit test.

1.1.3 The procedure for calculating the plasticity index is given in Section 19.

1.2 The liquid limit and plastic limit of soils (along with the shrinkage limit) are often collectively referred to as the Atterberg limits in recognition of their formation by Swedish soil scientist, A. Atterberg. These limits distinguish the boundaries of the several consistency states of plastic soils.

1.3 As used in this test method, soil is any natural aggregation of mineral or organic materials, mixtures of such materials, or artificial mixtures of aggregates and natural mineral and organic particles.

1.4 The multipoint liquid limit procedure is somewhat more time consuming than the one-point procedure when both are performed by experienced operators. However, the one-point procedure requires the operator to judge when the test specimen is approximately at its liquid limit. In cases where this is not done reliably, the multipoint procedure is as fast as the one-point procedure and provides additional precision due to the information obtained from additional trials. It is particularly recommended that the multipoint procedure be used by inexperienced operators.

1.5 The correlations on which the calculations of the one-point procedure are based may not be valid for certain soils, such as organic soils or

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[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity and Density Characteristics of Soils.

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soils from a marine environment. The liquid limit of these soils should therefore be determined by the multipoint procedure (Procedure A).

1.6 The liquid and plastic limits of many soils that have been allowed to dry before testing may be considerably different from values obtained on undried samples. If the liquid and plastic limits of soils are used to correlate or estimate the engineering behavior of soils in their natural moist state, samples should not be permitted to dry before testing unless data on dried samples are specifically desired.

1.7 The composition and concentration of soluble salts in a soil affect the values of the liquid and plastic limits as well as the water content values of soils (see Method D 2216). Special consideration should therefore be given to soils from a marine environment or other sources where high soluble salt concentrations may be present. The degree to which the salts present in these soils are diluted or concentrated must be given consideration if meaningful results are to be obtained.

1.8 Since the tests described herein are performed only on that portion of a soil which passes the 425-μm (No. 40) sieve, the relative contribution of this portion of the soil to the properties of the sample as a whole must be considered when using these tests to evaluate the properties of a soil.

1.9 The values stated in acceptable metric units are to be regarded as the standard. The values given in parentheses are for information only.

1.10 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Applicable Documents

2.1 *ASTM Standards:*

C 702 Methods for Reducing Field Samples of Aggregate to Testing Size[2]

D 75 Practice for Sampling Aggregates[3]

D 420 Recommended Practice for Investigating and Sampling Soil and Rock for Engineering Purposes[4]

D 653 Terms and Symbols Relating to Soil and Rock[4]

D 1241 Specification for Materials for Soil-Aggregate Subbase, Base, and Surface Courses[4]

D 2216 Method for Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil-Aggregate Mixtures[4]

D 2240 Test Method for Rubber Property—Durometer Hardness[5]

D 2487 Test Method for Classification of Soils for Engineering Purposes[4]

D 2488 Practice for Description and Identification of Soils (Visual-Manual Procedure)[4]

D 3282 Practice for Classification of Soils and Soil-Aggregate Mixtures for Highway Construction Purposes[4]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[6]

E 319 Methods of Testing Single-Arm Balances[6]

E 898 Method of Testing Top-Loading, Direct-Reading Laboratory Scales and Balances[6]

3. Definitions

3.1 *Atterberg limits*—originally, seven "limits of consistency" of fine-grained soils were defined by Albert Atterberg. In current engineering usage, the term usually refers only to the liquid limit, plastic limit, and in some references, the shrinkage limit.

3.2 *consistency*—the relative ease with which a soil can be deformed.

3.3 *liquid limit (LL)*—the water content, in percent, of a soil at the arbitrarily defined boundary between the liquid and plastic states. This water content is defined as the water content at which a pat of soil placed in a standard cup and cut by a groove of standard dimensions will flow together at the base of the groove for a distance of 13 mm (½ in.) when subjected to 25 shocks from the cup being dropped 10 mm in a standard liquid limit apparatus operated at a rate of 2 shocks per second.

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[2] *Annual Book of ASTM Standards*, Vol 04.02.

[3] *Annual Book of ASTM Standards*, Vols 04.02, 04.03, and 04.08.

[4] *Annual Book of ASTM Standards*, Vol 04.08.

[5] *Annual Book of ASTM Standards*, Vol 09.01.

[6] *Annual Book of ASTM Standards*, Vol 14.02.

NOTE 2—The undrained shear strength of soil at the liquid limit is considered to be 2 ±0.2 kPa (0.28 psi).

3.4 *plastic limit (PL)*—the water content, in percent, of a soil at the boundary between the plastic and brittle states. The water content at this boundary is the water content at which a soil can no longer be deformed by rolling into 3.2 mm (⅛ in.) in diameter threads without crumbling.

3.5 *plastic soil*—a soil which has a range of water content over which it exhibits plasticity and which will retain its shape on drying.

3.6 *plasticity index (PI)*—the range of water content over which a soil behaves plastically. Numerically, it is the difference between the liquid limit and the plastic limit.

3.7 *liquidity index*—the ratio, expressed as a percentage, of (*1*) the natural water content of a soil minus its plastic limit, to (*2*) its plasticity index.

3.8 *activity number (A)*—the ratio of (*1*) the plasticity index of a soil to (*2*) the percent by weight of particles having an equivalent diameter smaller than 0.002 mm.

4. Summary of Method

4.1 The sample is processed to remove any material retained on a 425-μm (No. 40) sieve. The liquid limit is determined by performing trials in which a portion of the sample is spread in a brass cup, divided in two by a grooving tool, and then allowed to flow together from the shocks caused by repeatedly dropping the cup in a standard mechanical device. The multipoint liquid limit, Procedures A and B, requires three or more trials over a range of water contents to be performed and the data from the trials plotted or calculated to make a relationship from which the liquid limit is determined. The one-point liquid limit, Procedures C and D, uses the data from two trials at one water content multiplied by a correction factor to determine the liquid limit.

4.2 The plastic limit is determined by alternately pressing together and rolling into a 3.2 mm (⅛ in.) diameter thread a small portion of plastic soil until its water content is reduced to a point at which the thread crumbles and is no longer able to be pressed together and rerolled. The water content of the soil at this stage is reported as the plastic limit.

4.3 The plasticity index is calculated as the difference between the liquid limit and the plastic limit.

5. Significance and Use

5.1 This test method is used as an integral part of several engineering classification systems to characterize the fine-grained fractions of soils (see Test Method D 2487 and Practice D 3282) and to specify the fine-grained fraction of construction materials (see Specification D 1241). The liquid limit, plastic limit, and plasticity index of soils are also used extensively, either individually or together with other soil properties to correlate with engineering behavior such as compressibility, permeability, compactibility, shrink-swell, and shear strength.

5.2 The liquid and plastic limits of a soil can be used with the natural water content of the soil to express its relative consistency or liquidity index and can be used with the percentage finer than 2-μm size to determine its activity number.

5.3 The one-point liquid limit procedure is frequently used for routine classification purposes. When greater precision is required, as when used for the acceptance of a material or for correlation with other test data, the multipoint procedure should be used.

5.4 These methods are sometimes used to evaluate the weathering characteristics of clay-shale materials. When subjected to repeated wetting and drying cycles, the liquid limits of these materials tend to increase. The amount of increase is considered to be a measure of a shale's susceptibility to weathering.

5.5 The liquid limit of a soil containing substantial amounts of organic matter decreases dramatically when the soil is oven-dried before testing. Comparison of the liquid limit of a sample before and after oven-drying can therefore be used as a qualitative measure of organic matter content of a soil.

6. Apparatus

6.1 *Liquid Limit Device*—A mechanical device consisting of a brass cup suspended from a carriage designed to control its drop onto a hard rubber base. A drawing showing the essential features of the device and the critical dimensions is given in Fig. 1. The design of the device may vary provided that the essential functions are

preserved. The device may be operated either by a hand crank or by an electric motor.

6.1.1 *Base*—The base shall be hard rubber having a D Durometer hardness of 80 to 90, and a resilience such that an 8-mm (5/16-in.) diameter polished steel ball, when dropped from a height of 25 cm (9.84 in.) will have an average rebound of at least 80 % but no more than 90 %. The tests shall be conducted on the finished base with feet attached.

6.1.2 *Feet*—The base shall be supported by rubber feet designed to provide isolation of the base from the work surface and having an A Durometer hardness no greater than 60 as measured on the finished feet attached to the base.

6.1.3 *Cup*—The cup shall be brass and have a weight, including cup hanger, of 185 to 215 g.

6.1.4 *Cam*—The cam shall raise the cup smoothly and continuously to its maximum height, over a distance of at least 180° of cam rotation. The preferred cam motion is a uniformly accelerated lift curve. The design of the cam and follower combination shall be such that there is no upward or downward velocity of the cup when the cam follower leaves the cam.

NOTE 3—The cam and follower design in Fig. 1 is for uniformly accelerated (parabolic) motion after contact and assures that the cup has no velocity at drop off. Other cam designs also provide this feature and may be used. However, if the cam-follower lift pattern is not known, zero velocity at drop off can be assured by carefully filing or machining the cam and follower so that the cup height remains constant over the last 20 to 45° of cam rotation.

6.1.5 *Carriage*—The cup carriage shall be constructed in a way that allows convenient but secure adjustment of the height of drop of the cup to 10 mm (0.394 in.). The cup hanger shall be attached to the carriage by means of a pin which allows removal of the cup and cup hanger for cleaning and inspection.

6.1.6 *Optional Motor Drive*—As an alternative to the hand crank shown in Fig. 1, the device may be equipped with a motor to turn the cam. Such a motor must turn the cam at 2 ±0.1 revolutions per second, and must be isolated from the rest of the device by rubber mounts or in some other way that prevents vibration from the motor being transmitted to the rest of the apparatus. It must be equipped with an ON-OFF switch and a means of conveniently positioning the cam for height of drop adjustments. The results obtained using a motor-driven device must not differ from those obtained using a manually operated device.

6.2 *Flat Grooving Tool*—A grooving tool having dimensions shown in Fig. 2. The tool shall be made of plastic or noncorroding metal. The design of the tool may vary as long as the essential dimensions are maintained. The tool may, but need not, incorporate the gage for adjusting the height of drop of the liquid limit device.

6.3 *Gage*—A metal gage block for adjusting the height of drop of the cup, having the dimensions shown in Fig. 3. The design of the tool may vary provided the gage will rest securely on the base without being susceptible to rocking, and the edge which contacts the cup during adjustment is straight, at least 10 mm (3/8 in.) wide, and without bevel or radius.

6.4 *Containers*—Small corrosion-resistant containers with snug-fitting lids for water content specimens. Aluminum or stainless steel cans 2.5 cm (1 in.) high by 5 cm (2 in.) in diameter are appropriate.

6.5 *Balance*—A balance readable to at least 0.01 g and having an accuracy of 0.03 g within three standard deviations within the range of use. Within any 15-g range, a difference between readings shall be accurate within 0.01 g (Notes 4 and 5).

NOTE 4—See Methods E 898 and E 319 for an explanation of terms relating to balance performance.

NOTE 5—For frequent use, a top-loading type balance with automatic load indication, readable to 0.01 g, and having an index of precision (standard deviation) of 0.003 or better is most suitable for this method. However, nonautomatic indicating equal-arm analytical balances and some small equal arm top pan balances having readabilities and sensitivities of 0.002 g or better provide the required accuracy when used with a weight set of ASTM Class 4 (National Bureau of Standards Class P) or better. Ordinary commercial and classroom type balances such as beam balances are not suitable for this method.

6.6 *Storage Container*—A container in which to store the prepared soil specimen that will not contaminate the specimen in any way, and which prevents moisture loss. A porcelain, glass, or plastic dish about 11.4 cm (4½ in.) in diameter and a plastic bag large enough to enclose the dish and be folded over is adequate.

6.7 *Ground Glass Plate*—A ground glass plate at least 30 cm (12 in.) square by 1 cm (3/8 in.) thick for mixing soil and rolling plastic limit threads.

6.8 *Spatula*—A spatula or pill knife having a

blade about 2 cm (¾ in.) wide by about 10 cm (4 in.) long. In addition, a spatula having a blade about 2.5 cm (1 in.) wide and 15 cm (6 in.) long has been found useful for initial mixing of samples.

6.9 *Sieve*—A 20.3 cm (8 in.) diameter, 425-μm (No. 40) sieve conforming to the requirements of Specification E 11 and having a rim at least 5 cm (2 in.) above the mesh. A 2-mm (No. 10) sieve meeting the same requirements may also be needed.

6.10 *Wash Bottle*, or similar container for adding controlled amounts of water to soil and washing fines from coarse particles.

6.11 *Drying Oven*—A thermostatically controlled oven, preferably of the forced-draft type, capable of continuously maintaining a temperature of 110 ±5°C throughout the drying chamber. The oven shall be equipped with a thermometer of suitable range and accuracy for monitoring oven temperature.

6.12 *Washing Pan*—A round, flat-bottomed pan at least 7.6 cm (3 in.) deep, slightly larger at the bottom than a 20.3-cm (8-in.) diameter sieve.

6.13 *Rod* (optional)—A metal or plastic rod or tube 3.2 mm (⅛ in.) in diameter and about 10 cm (4 in.) long for judging the size of plastic limit threads.

7. Materials

7.1 A supply of distilled or demineralized water.

8. Sampling

8.1 Samples may be taken from any location that satisfies testing needs. However, Methods C 702, and Practice D 75, and Recommended Practice D 420 should be used as guides for selecting and preserving samples from various types of sampling operations. Samples which will be prepared using the wet preparation procedure, 10.1, must be kept at their natural water content prior to preparation.

8.2 Where sampling operations have preserved the natural stratification of a sample, the various strata must be kept separated and tests performed on the particular stratum of interest with as little contamination as possible from other strata. Where a mixture of materials will be used in construction, combine the various components in such proportions that the resultant sample represents the actual construction case.

8.3 Where data from this test method are to be used for correlation with other laboratory or field test data, use the same material as used for these tests where possible.

8.4 Obtain a representative portion from the total sample sufficient to provide 150 to 200 g of material passing the 425-μm (No. 40) sieve. Free flowing samples may be reduced by the methods of quartering or splitting. Cohesive samples shall be mixed thoroughly in a pan with a spatula, or scoop and a representative portion scooped from the total mass by making one or more sweeps with a scoop through the mixed mass.

9. Calibration of Apparatus

9.1 *Inspection of Wear:*

9.1.1 *Liquid Limit Device*—Determine that the liquid limit device is clean and in good working order. The following specific points should be checked:

9.1.1.1 *Wear of Base*—The spot on the base where the cup makes contact should be worn no greater than 10 mm (⅜ in.) in diameter. If the wear spot is greater than this, the base can be machined to remove the worn spot provided the resurfacing does not make the base thinner than specified in 6.1 and the other dimensional relationships are maintained.

9.1.1.2 *Wear of Cup*—The cup must be replaced when the grooving tool has worn a depression in the cup 0.1 mm (0.004 in.) deep or when the edge of the cup has been reduced to half its original thickness. Verify that the cup is firmly attached to the cup hanger.

9.1.1.3 *Wear of Cup Hanger*—Verify that the cup hanger pivot does not bind and is not worn to an extent that allows more than 3-mm (⅛-in.) side-to-side movement of the lowest point on the rim.

9.1.1.4 *Wear of Cam*—The cam shall not be worn to an extent that the cup drops before the cup hanger (cam follower) loses contact with the cam.

9.1.2 *Grooving Tools*—Inspect grooving tools for wear on a frequent and regular basis. The rapidity of wear depends on the material from which the tool is made and the types of soils being tested. Sandy soils cause rapid wear of grooving tools; therefore, when testing these materials, tools should be inspected more frequently than for other soils. Any tool with a tip width greater than 2.1 mm must not be used. The depth

of the tip of the grooving tool must be 7.9 to 8.1 mm.

NOTE 6—The width of the tip of grooving tools is conveniently checked using a pocket-sized measuring magnifier equipped with a millimetre scale. Magnifiers of this type are available from most laboratory supply companies. The depth of the tip of grooving tools can be checked using the depth measuring feature of vernier calipers.

9.2 *Adjustment of Height of Drop*—Adjust the height of drop of the cup so that the point on the cup that comes in contact with the base rises to a height of 10 ±0.2 mm. See Fig. 4 for proper location of the gage relative to the cup during adjustment.

NOTE 7—A convenient procedure for adjusting the height of drop is as follows: place a piece of masking tape across the outside bottom of the cup parallel with the axis of the cup hanger pivot. The edge of the tape away from the cup hanger should bisect the spot on the cup that contacts the base. For new cups, placing a piece of carbon paper on the base and allowing the cup to drop several times will mark the contact spot. Attach the cup to the device and turn the crank until the cup is raised to its maximum height. Slide the height gage under the cup from the front, and observe whether the gage contacts the cup or the tape. See Fig. 4. If the tape and cup are both contacted, the height of drop is approximately correct. If not, adjust the cup until simultaneous contact is made. Check adjustment by turning the crank at 2 revolutions per second while holding the gage in position against the tape and cup. If a ringing or clicking sound is heard without the cup rising from the gage, the adjustment is correct. If no ringing is heard or if the cup rises from the gage, readjust the height of drop. If the cup rocks on the gage during this checking operation, the cam follower pivot is excessively worn and the worn parts should be replaced. Always remove tape after completion of adjustment operation.

MULTIPOINT LIQUID LIMIT—PROCEDURES A AND B

10. Preparation of Test Specimens

10.1 *Wet Preparation*—Except where the dry method of specimen preparation is specified (10.2), prepare specimens for test as described in the following sections.

10.1.1 *Samples Passing the 425-μm (No. 40) Sieve*—When by visual and manual procedures it is determined that the sample has little or no material retained on a 425-μm (No. 40) sieve, prepare a specimen of 150 to 200 g by mixing thoroughly with distilled or demineralized water on the glass plate using the spatula. If desired, soak soil in a storage dish with small amount of water to soften the soil before the start of mixing. Adjust the water content of the soil to bring it to a consistency that would require 25 to 35 blows of the liquid limit device to close the groove (Note 8). If, during mixing, a small percentage of material is encountered that would be retained on a 425-μm (No. 40) sieve, remove these particles by hand, if possible. If it is impractical to remove the coarser material by hand, remove small percentages (less than about 15 %) of coarser material by working the specimen through a 425-μm (No. 40) sieve using a piece of rubber sheeting, rubber stopper, or other convenient device provided the operation does not distort the sieve or degrade material that would be retained if the washing method described in 10.1.2 were used. If larger percentages of coarse material are encountered during mixing, or it is considered impractical to remove the coarser material by the methods just described, wash the sample as described in 10.1.2. When the coarse particles found during mixing are concretions, shells, or other fragile particles, do not crush these particles to make them pass a 425-μm (No. 40) sieve, but remove by hand or by washing. Place the mixed soil in the storage dish, cover to prevent loss of moisture, and allow to stand for at least 16 h (overnight). After the standing period and immediately before starting the test, thoroughly remix the soil.

NOTE 8—The time taken to adequately mix a soil will vary greatly, depending on the plasticity and initial water content. Initial mixing times of more than 30 — in may be needed for stiff, fat clays.

10.1.2 *Samples Containing Material Retained on a 425-μm (No. 40) Sieve:*

10.1.2.1 Select a sufficient quantity of soil at natural water content to provide 150 to 200 g of material passing the 425-μm (No. 40) sieve. Place in a pan or dish and add sufficient water to cover the soil. Allow to soak until all lumps have softened and the fines no longer adhere to the surfaces of the corase particles (Note 9).

NOTE 9—In some cases, the cations of salts present in tap water will exchange with the natural cations in the soil and significantly alter the test results should tap water be used in the soaking and washing operations. Unless it is known that such cations are not present in the tap water, distilled or demineralized water should be used. As a general rule, water containing more than 100 mg/L of dissolved solids should not be used for washing operations.

10.1.2.2 When the sample contains a large percentage of material retained on the 425-μm

(No. 40) sieve, perform the following washing operation in increments, washing no more than 0.5 kg (1 lb) of material at one time. Place the 425-μm (No. 40) sieve in the bottom of the clean pan. Pour the soil water mixture onto the sieve. If gravel or coarse sand particles are present, rinse as many of these as possible with small quantities of water from a wash bottle, and discard. Alternatively, pour the soil water mixture over a 2-mm (No. 10) sieve nested atop the 425-μm (No. 40) sieve, rinse the fine material through and remove the 2-mm (No. 10) sieve. After washing and removing as much of the coarser material as possible, add sufficient water to the pan to bring the level to about 13 mm (½ in.) above the surface of the 425-μm (No. 40) sieve. Agitate the slurry by stirring with the fingers while raising and lowering the sieve in the pan and swirling the suspension so that fine material is washed from the coarser particles. Disaggregate fine soil lumps that have not slaked by gently rubbing them over the sieve with the fingertips. Complete the washing operation by raising the sieve above the water surface and rinsing the material retained with a small amount of clean water. Discard material retained on the 425-μm (No. 40) sieve.

10.1.2.3 Reduce the water content of the material passing the 425-μm (No. 40) sieve until it approaches the liquid limit. Reduction of water content may be accomplished by one or a combination of the following methods: (*a*) exposing the air currents at ordinary room temperature, (*b*) exposing to warm air currents from a source such as an electric hair dryer, (*c*) filtering in a Buckner funnel or using filter candles, (*d*) decanting clear water from surface of suspension, or (*e*) draining in a colander or plaster of paris dish lined with high retentivity, high wet-strength filter paper.[7] If a plaster of paris dish is used, take care that the dish never becomes sufficiently saturated that it fails to actively absorb water into its surface. Thoroughly dry dishes between uses. During evaporation and cooling, stir the sample often enough to prevent overdrying of the fringes and soil pinnacles on the surface of the mixture. For soil samples containing soluble salts, use a method of water reduction such as *a* or *b* that will not eliminate the soluble salts from the test specimen.

10.1.2.4 Thoroughly mix the material passing the 425-μm (No. 40) sieve on the glass plate using the spatula. Adjust the water content of the mixture, if necessary, by adding small increments of distilled or demineralized water or by allowing the mixture to dry at room temperature while mixing on the glass plate. The soil should be at a water content that will result in closure of the groove in 25 to 35 blows. Return the mixed soil to the mixing dish, cover to prevent loss of moisture, and allow to stand for at least 16 h. After the standing period, and immediately before starting the test, remix the soil thoroughly.

10.2 *Dry Preparation:*

10.2.1 Select sufficient soil to provide 150 to 200 g of material passing the 425-μm (No. 40) sieve after processing. Dry the sample at room temperature or in an oven at a temperature not exceeding 60°C until the soil clods will pulverize readily. Disaggregation is expedited if the sample is not allowed to completely dry. However, the soil should have a dry appearance when pulverized. Pulverize the sample in a mortar with a rubber tipped pestal or in some other way that does not cause breakdown of individual grains. When the coarse particles found during pulverization are concretions, shells, or other fragile particles, do not crush these particles to make them pass a 425-μm (No. 40) sieve, but remove by hand or other suitable means, such as washing.

10.2.2 Separate the sample on a 425-μm (No. 40) sieve, shaking the sieve by hand to assure thorough separation of the finer fraction. Return the material retained on the 425-μm (No. 40) sieve to the pulverizing apparatus and repeat the pulverizing and sieving operations as many times as necessary to assure that all finer material has been disaggregated and material retained on the 425-μm (No. 40) sieve consists only of individual sand or gravel grains.

10.2.3 Place material remaining on the 425-μm (No. 40) sieve after the final pulverizing operations in a dish and soak in a small amount of water. Stir the soil water mixture and pour over the 425-μm (No. 40) sieve, catching the water and any suspended fines in the washing pan. Pour this suspension into a dish containing the dry soil previously sieved through the 425-μm (No. 40) sieve. Discard material retained on the 425-μm (No. 40) sieve.

10.2.4 Adjust the water content as necessary by drying as described in 10.1.2.3 or by mixing on the glass plate, using the spatula while adding increments of distilled or demineralized water,

[7] S and S 595 filter paper, available in 32-cm circles, has proven satisfactory.

until the soil is at a water content that will result in closure of the groove in 25 to 35 blows.

10.2.5 Put soil in the storage dish, cover to prevent loss of moisture and allow to stand for at least 16 h. After the standing period, and immediately before starting the test, thoroughly remix the soil (Note 8).

11. Procedure

11.1 Place a portion of the prepared soil in the cup of the liquid limit device at the point where the cup rests on the base, squeeze it down, and spread it into the cup to a depth of about 10 mm at its deepest point, tapering to form an approximately horizontal surface. Take care to eliminate air bubbles from the soil pat but form the pat with as few strokes as possible. Heap the unused soil on the glass plate and cover with the inverted storage dish or a wet towel.

11.2 Form a groove in the soil pat by drawing the tool, beveled edge forward, through the soil on a line joining the highest point to the lowest point on the rim of the cup. When cutting the groove, hold the grooving tool against the surface of the cup and draw in an arc, maintaining the tool perpendicular to the surface of the cup throughout its movement. See Fig. 5. In soils where a groove cannot be made in one stroke without tearing the soil, cut the groove with several strokes of the grooving tool. Alternatively, cut the groove to slightly less than required dimensions with a spatula and use the grooving tool to bring the groove to final dimensions. Exercise extreme care to prevent sliding the soil pat relative to the surface of the cup.

11.3 Verify that no crumbs of soil are present on the base or the underside of the cup. Lift and drop the cup by turning the crank at a rate of 1.9 to 2.1 drops per second until the two halves of the soil pat come in contact at the bottom of the groove along a distance of 13 mm (½ in.). See Fig. 6.

NOTE 10—Use the end of the grooving tool, Fig. 2, or a scale to verify that the groove has closed 13 mm (½ in.).

11.4 Verify that an air bubble has not caused premature closing of the groove by observing that both sides of the groove have flowed together with approximately the same shape. If a bubble has caused premature closing of the groove, reform the soil in the cup, adding a small amount of soil to make up for that lost in the grooving operation and repeat 11.1 to 11.3. If the soil slides on the surface of the cup, repeat 11.1 through 11.3 at a higher water content. If, after several trials at successively higher water contents, the soil pat continues to slide in the cup or if the number of blows required to close the groove is always less than 25, record that the liquid limit could not be determined, and report the soil as nonplastic without performing the plastic limit test.

11.5 Record the number of drops, N, required to close the groove. Remove a slice of soil approximately the width of the spatula, extending from edge to edge of the soil cake at right angles to the groove and including that portion of the groove in which the soil flowed together, place in a weighed container, and cover.

11.6 Return the soil remaining in the cup to the glass plate. Wash and dry the cup and grooving tool and reattach the cup to the carriage preparation for the next trial.

11.7 Remix the entire soil specimen on the glass plate adding distilled water to increase the water content of the soil and decrease the number of blows required to close the groove. Repeat 11.1 through 11.6 for at least two additional trials producing successively lower numbers of blows to close the groove. One of the trials shall be for a closure requiring 25 to 35 blows, one for closure between 20 and 30 blows, and one trial for a closure requiring 15 to 25 blows.

11.8 Determine the water content, W_N, of the soil specimen from each trial in accordance with Method D 2216. Make all weighings on the sar balance. Initial weighings should be performed immediately after completion of the test. If the test is to be interrupted for more than about 15 min, the specimens already obtained should be weighed at the time of the interruption.

12. Calculations

12.1 Plot the relationship between the water content, W_N, and the corresponding number of drops, N, of the cup on a semilogarithmic graph with the water content as ordinates on the arithmetical scale, and the number of drops as abscissas on the logarithmic scale. Draw the best straight line through the three or more plotted points.

12.2 Take the water content corresponding to the intersection of the line with the 25-drop abscissa as the liquid limit of the soil. Computa-

tional methods may be substituted for the graphical method for fitting a straight line to the data and determining the liquid limit.

ONE-POINT LIQUID LIMIT—PROCEDURES C AND D

13. Preparation of Test Specimens

13.1 Prepare the specimen in the same manner as described in Section 10, except that at mixing, adjust the water content to a consistency requiring 20 to 30 drops of the liquid limit cup to close the groove.

14. Procedure

14.1 Proceed as described in 11.1 through 11.5 except that the number of blows required to close the groove shall be 20 to 30. If less than 20 or more than 30 blows are required, adjust the water content of the soil and repeat the procedure.

14.2 Immediately after removing a water content specimen as described in 11.5, reform the soil in the cup, adding a small amount of soil to make up for that lost in the grooving and water content sampling operations. Repeat 11.2 through 11.5, and, if the second closing of the groove requires the same number of drops or no more than two drops difference, secure another water content specimen. Otherwise, remix the entire specimen and repeat.

NOTE 11—Excessive drying or inadequate mixing will cause the number of blows to vary.

14.3 Determine water contents of specimens as described in 11.8.

15. Calculations

15.1 Determine the liquid limit for each water content specimen using one of the following equations:

$$LL = W_N\left(\frac{N}{25}\right)^{0.121} \quad \text{or}$$

$$LL = K(W_N)$$

where:

N = the number of blows causing closure of the groove at water content,

W_N = water content, and

K = a factor given in Table 1.

The liquid limit is the average of the two trial liquid limit values.

15.2 If the difference between the two trial liquid limit values is greater than one percentage point, repeat the test.

PLASTIC LIMIT

16. Preparation of Test Specimen

16.1 Select a 20-g portion of soil from the material prepared for the liquid limit test, either after the second mixing before the test, or from the soil remaining after completion of the test. Reduce the water content of the soil to a consistency at which it can be rolled without sticking to the hands by spreading and mixing continuously on the glass plate. The drying process may be accelerated by exposing the soil to the air current from an electric fan, or by blotting with paper that does not add any fiber to the soil, such as hard surface paper toweling or high wet strength filter paper.

17. Procedure

17.1 From the 20-g mass, select a portion of 1.5 to 2.0 g. Form the test specimen into an ellipsoidal mass. Roll this mass between the palm or fingers and the ground-glass plate with just sufficient pressure to roll the mass into a thread of uniform diameter throughout its length (Note 12). The thread shall be further deformed on each stroke so that its diameter is continuously reduced and its length extended until the diameter reaches 3.2 ±0.5 mm (0.125 ±.020 in.), taking no more than 2 min (Note 13). The amount of hand or finger pressure required will vary greatly, according to the soil. Fragile soils of low plasticity are best rolled under the outer edge of the palm or at the base of the thumb.

NOTE 12—A normal rate of rolling for most soils should be 80 to 90 strokes per minute, counting a stroke as one complete motion of the hand forward and back to the starting position. This rate of rolling may have to be decreased for very fragile soils.

NOTE 13—A 3.2-mm (⅛-in.) diameter rod or tube is useful for frequent comparison with the soil thread to ascertain when the thread has reached the proper diameter, especially for inexperienced operators.

17.1.1 When the diameter of the thread becomes 3.2 mm, break the thread into several pieces. Squeeze the pieces together, knead between the thumb and first finger of each hand, reform into an ellipsoidal mass, and reroll. Continue this alternate rolling to a thread 3.2 mm in diameter, gathering together, kneading and rerolling, until the thread crumbles under the pres-

sure required for rolling and the soil can no longer be rolled into a 3.2-mm diameter thread (See Fig. 7). It has no significance if the thread breaks into threads of shorter length. Roll each of these shorter threads to 3.2 mm in diameter. The only requirement for continuing the test is that they are able to be reformed into an ellipsoidal mass and rolled out again. The operator shall at no time attempt to produce failure at exactly 3.2 mm diameter by allowing the thread to reach 3.2 mm, then reducing the rate of rolling or the hand pressure, or both, while continuing the rolling without further deformation until the thread falls apart. It is permissible, however, to reduce the total amount of deformation for feebly plastic soils by making the initial diameter of the ellipsoidal mass nearer to the required 3.2-mm final diameter. If crumbling occurs when the thread has a diameter greater than 3.2 mm, this shall be considered a satisfactory end point, provided the soil has been previously rolled into a thread 3.2 mm in diameter. Crumbling of the thread will manifest itself differently with the various types of soil. Some soils fall apart in numerous small aggregations of particles, others may form an outside tubular layer that starts splitting at both ends. The splitting progresses toward the middle, and finally, the thread falls apart in many small platy particles. Fat clay soils require much pressure to deform the thread, particularly as they approach the plastic limit. With these soils, the thread breaks into a series of barrel-shaped segments about 3.2 to 9.5 mm (⅛ to ⅜ in.) in length.

17.2 Gather the portions of the crumbled thread together and place in a weighed container. Immediately cover the container.

17.3 Select another 1.5 to 2.0 g portion of soil from the original 20-g specimen and repeat the operations described in 17.1 and 17.2 until the container has at least 6 g of soil.

17.4 Repeat 17.1 through 17.3 to make another container holding at least 6 g of soil. Determine the water content, in percent, of the soil contained in the containers in accordance with Method D 2216. Make all weighings on the same balance.

NOTE 14—The intent of performing two plastic limit trials is to verify the consistency of the test results. It is acceptable practice to perform only one plastic limit trial when the consistency in the test results can be confirmed by other means.

18. Calculations

18.1 Compute the average of the two water contents. If the difference between the two water contents is greater than two percentage points, repeat the test. The plastic limit is the average of the two water contents.

PLASTICITY INDEX

19. Calculations

19.1 Calculate the plasticity index as follows:

$$PI = LL - PL$$

where:

LL = the liquid limit,

PL = the plastic limit.

Both LL and PL are whole numbers. If either the liquid limit or plastic limit could not be determined, or if the plastic limit is equal to or greater than the liquid limit, report the soil a nonplastic, NP.

20. Report

20.1 Report the following information:

20.1.1 Sample identifying information,

20.1.2 Any special specimen selection process used, such as removal of sand lenses from undisturbed sample,

20.1.3 Report sample as airdried if the sample was airdried before or during preparation,

20.1.4 Liquid limit, plastic limit, and plasticity index to the nearest whole number and omitting the percent designation. If the liquid limit or plastic limit tests could not be performed, or the plastic limit is equal to or greater than the liquid limit, report the soil as nonplastic, NP,

20.1.5 An estimate of the percentage of sample retained on the 425-μm (No. 40) sieve, and

20.1.6 Procedure by which liquid limit was performed, if it differs from the multipoint method.

21. Precision and Bias

21.1 No interlaboratory testing program has as yet been conducted using this test method to determine multilaboratory precision.

21.2 The within laboratory precision of the results of tests performed by different operators at one laboratory on two soils using Procedure A for the liquid limit is shown in Table 2.

TABLE 1 Factors for Obtaining Liquid Limit from Water Content and Number of Drops Causing Closure of Groove

N (Number of Drops)	K (Factor for Liquid Limit)
20	0.974
21	0.979
22	0.985
23	0.990
24	0.995
25	1.000
26	1.005
27	1.009
28	1.014
29	1.018
30	1.022

TABLE 2 Within Laboratory Precision for Liquid Limit

	Average Value, $\bar{x}$	Standard Deviation, s
Soil A:		
PL	21.9	1.07
LL	27.9	1.07
Soil B:		
PL	20.1	1.21
LL	32.6	0.98

DIMENSIONS

LETTER	A △	B △	C △	E △	F	G	H	J △	K △	L △	M △
MM	54 ± 0.5	2 ± 0.1	27 ± 0.5	56 ± 2.0	32	10	16	60 ± 1.0	50 ± 2.0	150 ± 2.0	125 ± 2.0

LETTER	N	P	R	T	U △	V	W	Z
MM	24	28	24	45	47 ± 1.0	3.8	13	6.5

△ ESSENTIAL DIMENSIONS

CAM ANGLE DEGREES	CAM RADIUS
0	0.742 R
30	0.753 R
60	0.764 R
90	0.773 R
120	0.784 R
150	0.796 R
180	0.818 R
210	0.854 R
240	0.901 R
270	0.945R
300	0.974R
330	0.995R
360	1.000R

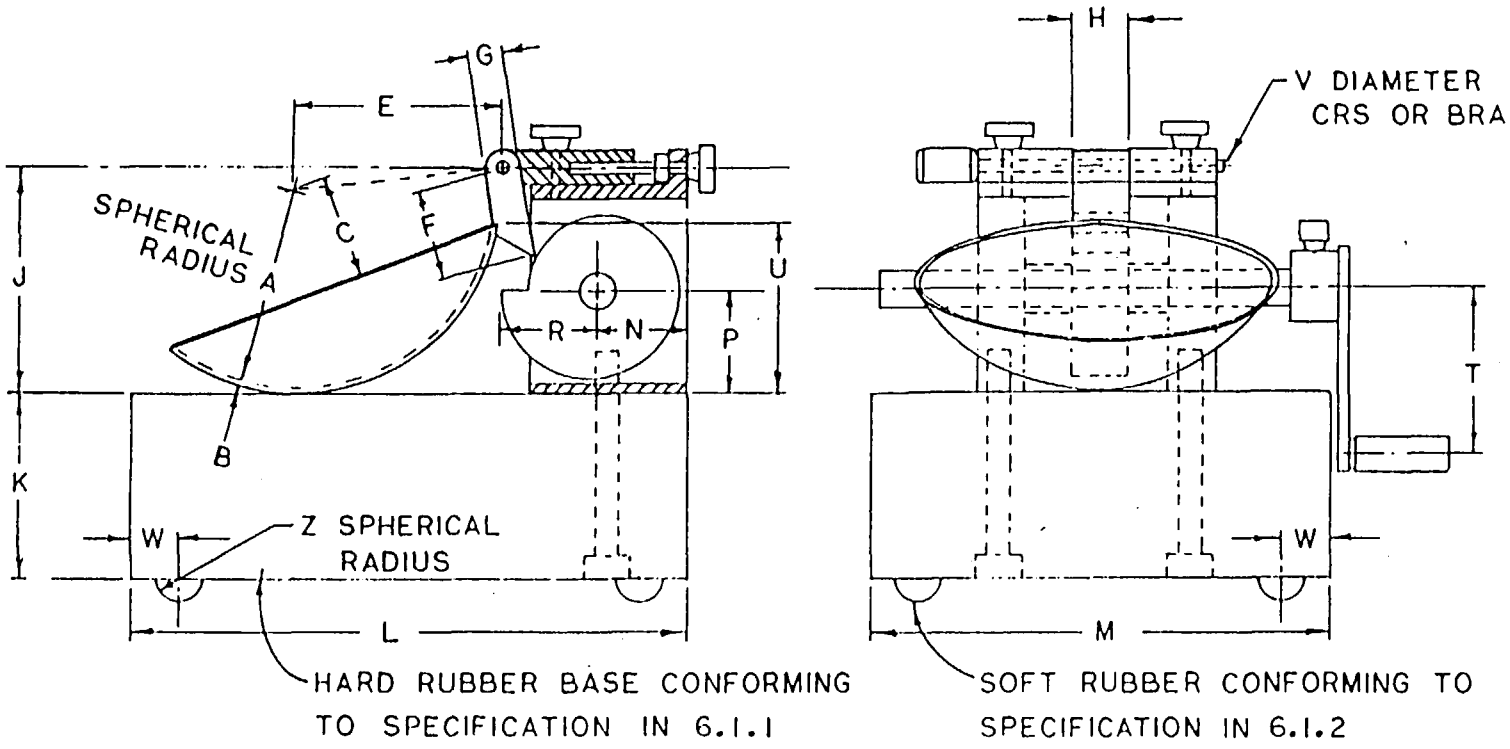


FIG. 1 Hand-Operated Liquid Limit Device

DIMENSIONS

LETTER	A △	B △	C △	D △	E △	F △
MM	2 ± 0.1	11 ± 0.2	40 ± 0.5	8 ± 0.1	50 ± 0.5	2 ± 0.1
LETTER	G	H	J	K △	L △	N
MM	10 MINIMUM	13	60	10 ±0.05	60 DEG ± 1 DEG	20

△ *ESSENTIAL DIMENSIONS*

□ *BACK AT LEAST 15 MM FROM TIP*

NOTE : DIMENSION A SHOULD BE 1.9–2.0 AND DIMENSION D SHOULD BE 8.0–8.1 WHEN NEW TO ALLOW FOR ADEQUATE SERVICE LIFE

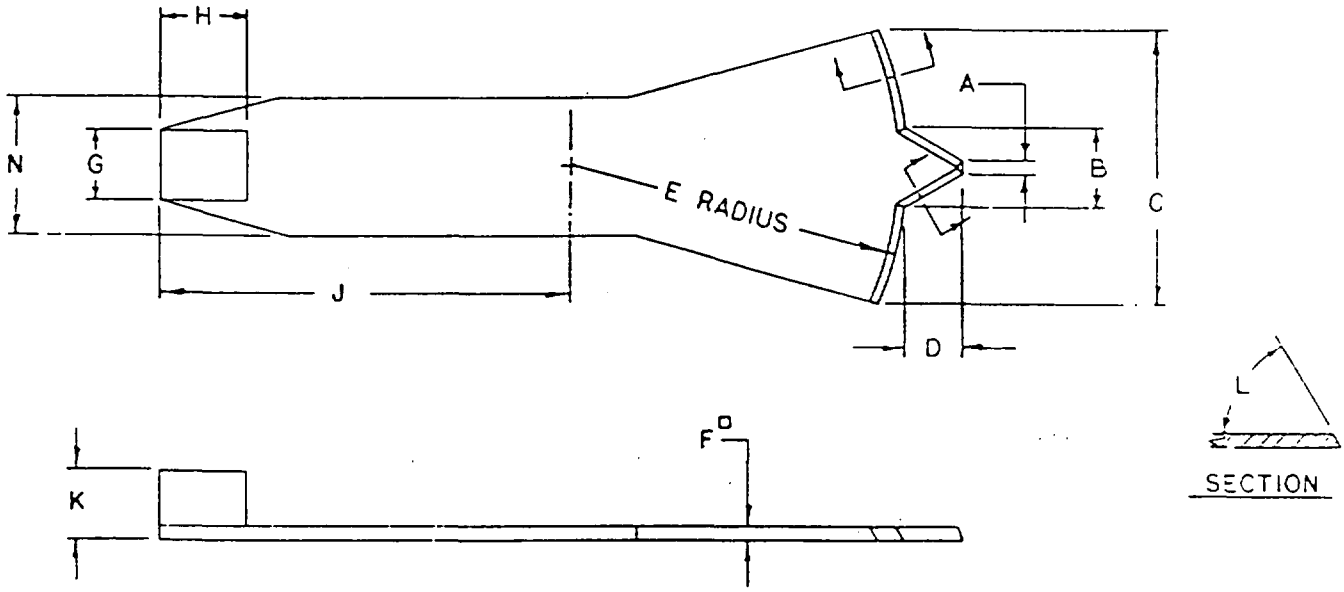
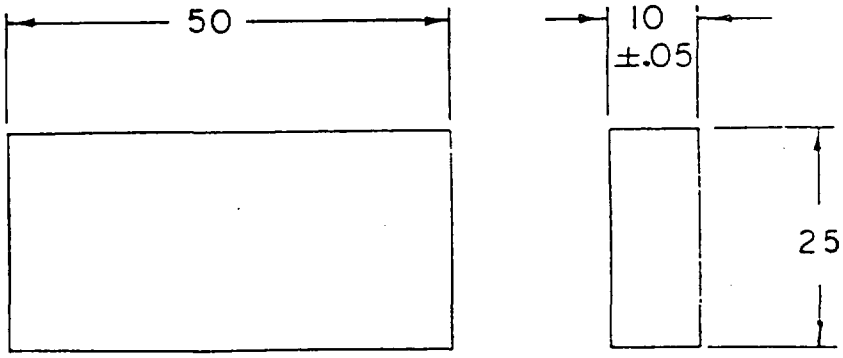


FIG. 2 Grooving Tool (Optional Height-of-Drop Gage Attached)



DIMENSIONS IN MILLIMETRES

FIG. 3 Height of Drop Gage

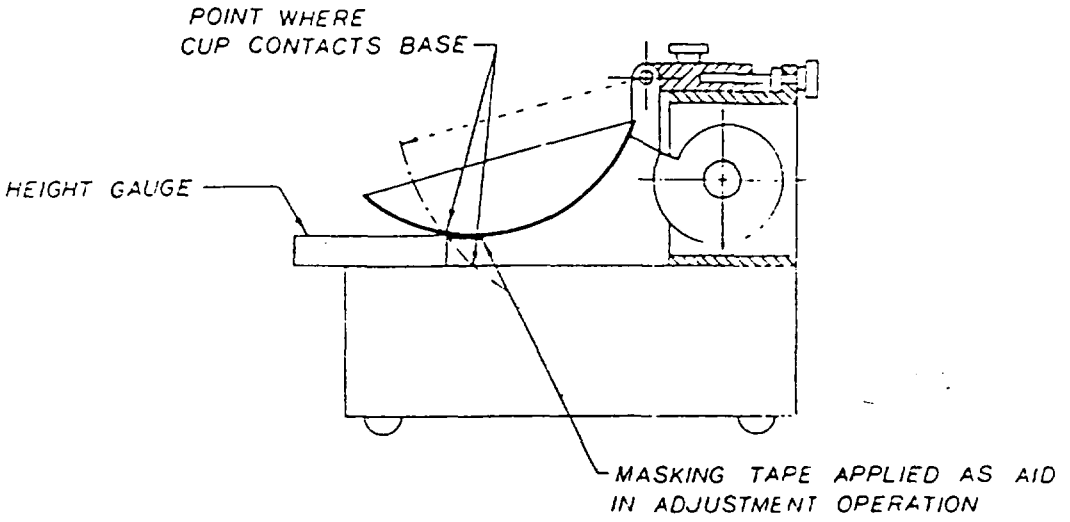


FIG. 4 Calibration for Height of Drop

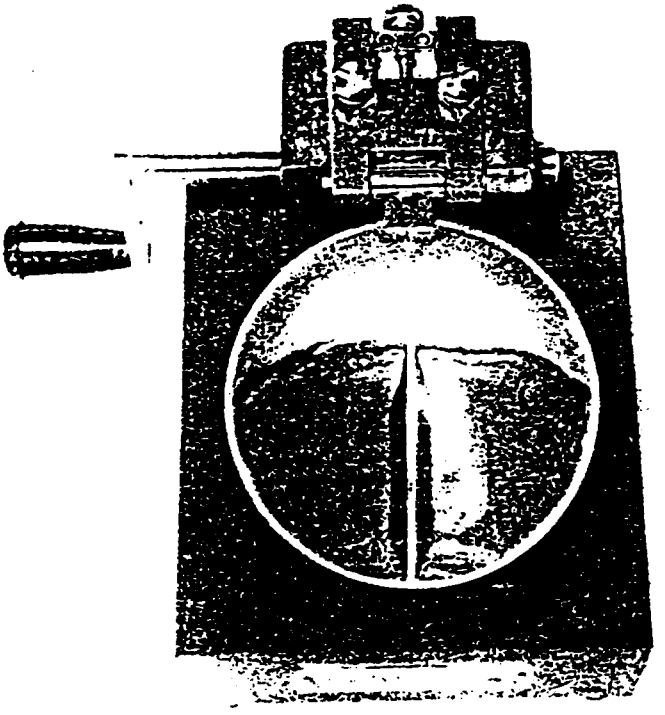


FIG. 5 Grooved Soil Pat in Liquid Limit Device

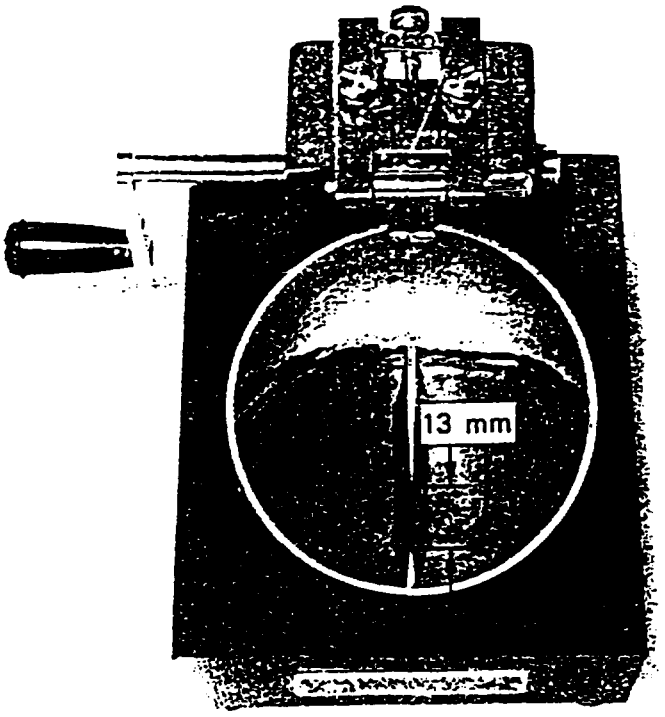


FIG. 6 Soil Pat After Groove Has Closed

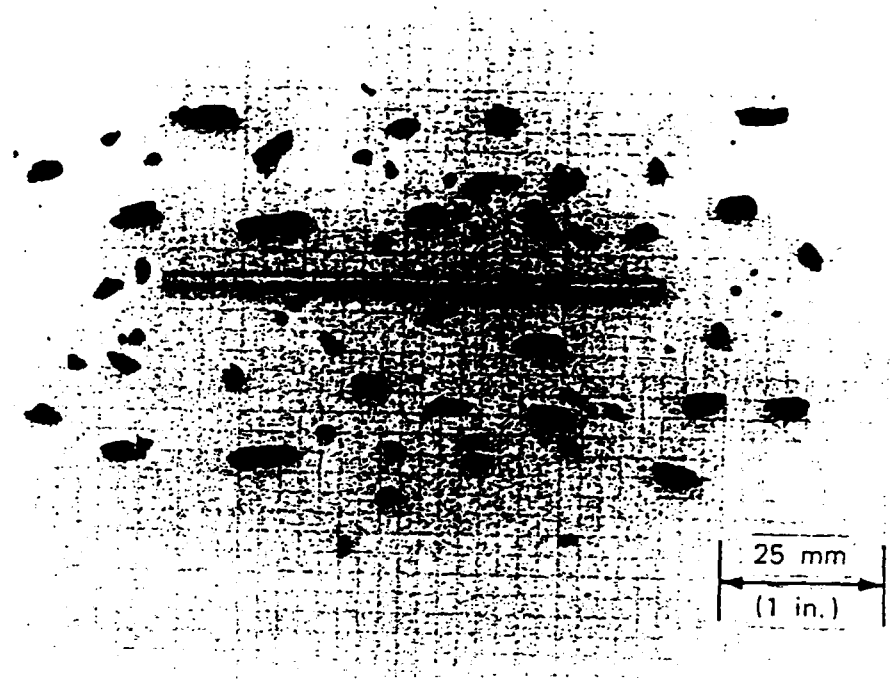


FIG. 7 Lean Clay Soil at the Plastic Limit

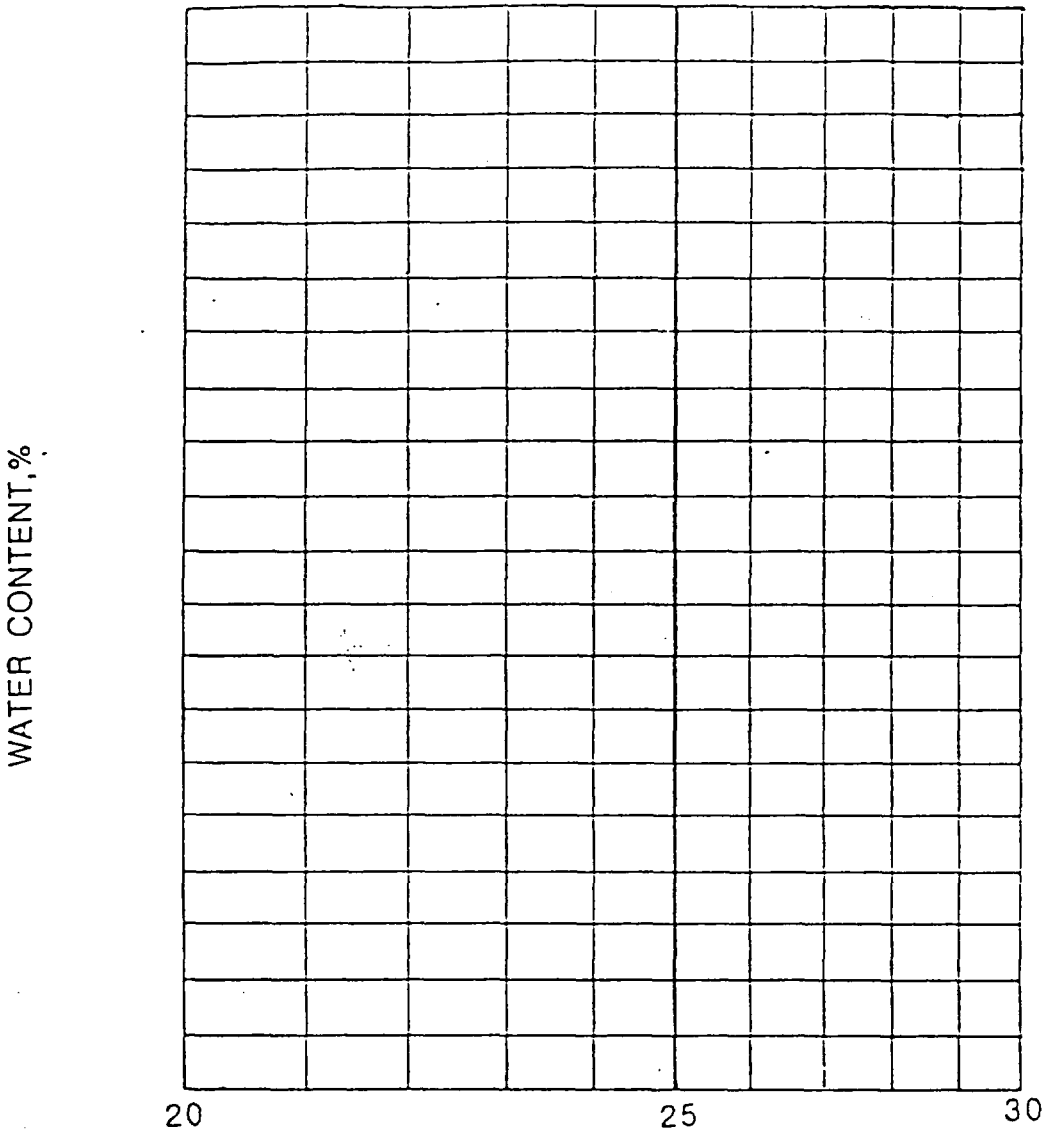
BY _____ DATE _____ JOB NAME _____ JOB NO. _____

CHECKED BY _____ SHEET _____ OF _____

SAMPLE NO.										
MATERIAL.										
UNCONFINED COMP. DIA, in.										
INITIAL HT, in.										
FINAL HT, in.										
MAX LOAD, lbs.										
Qa, tsf.										
Qu, tsf.										
UNIT WEIGHT DIA, in.										
LENGTH, in.										
WEIGHT, gms.										
NM										
DRY UNIT WEIGHT pcf.										
MOIST. CAN NO.										
WET WT, gms.										
DRY WT, gms.										
TARE, gms.										
% MOISTURE.										
CAN NO.										
WET WT, gms.										
DRY WT, gms.										
TARE, gms.										
BLOW MULT										
% MOISTURE.										
LIMIT CAN NO.										
WET WT, gms.										
DRY WT, gms.										
TARE. gms.										
% MOISTURE										
CUP NO.										
START WT, gms.										
END WT, gms.										
TARE, gms.										
% LOSS.										

REMARKS:

LIQUID LIMIT TEST



WARZYN

DWN	CHK'D	APP'D	DATE	

Designation: D 427 – 83[ε1]

Standard Test Method for SHRINKAGE FACTORS OF SOILS[1]

This standard is issued under the fixed designation D 427; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

[ε1] NOTE—Paragraph 6.3.1 was editorially added in April 1984.

1. Scope

1.1 This test method covers tests for obtaining the data from which the following subgrade soil constants may be calculated: shrinkage limit, shrinkage ratio, volumetric shrinkage, linear shrinkage, and specific gravity (approximate).

1.2 The values stated in inch-pound units are to be regarded as the standard.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precaution statements, see 6.3.1.

2. Applicable Document

2.1 *ASTM Standard:*

D421 Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

3. Significance and Use

3.1 The shrinkage factors covered in this test method can only be determined on basically fine-grained (cohesive) soils which exhibit a dry strength when oven dried.

3.2 The term "shrinkage limit", expressed as a water content in percent, is typically assumed to represent the amount of water required to fill the voids of a given cohesive soil at its minimum void ratio obtained by drying (usually oven). Thus, the concept shrinkage limit can be used to evaluate the shrinkage potential, or possibility of development, or both, of cracks in earthworks involving cohesive soils.

4. Apparatus

4.1 *Evaporating Dish*, porcelain, about 5½ in. (139.7 mm) in diameter.

4.2 *Spatula*, or pill knife having a blade about 3 in. (76.2 mm) in length and about ¾ in (19.0 mm) in width.

4.3 *Shrinkage Dish*—A circular porcelain or monel metal milk dish having a flat bottom and being about 1¾ in. (44.4 mm) in diameter and about ½ in. (12.7 mm) in height.

4.4 *Straightedge*, steel, about 6 in. (150 mm) in length.

4.5 *Glass Cup*, about 2¼ in. (57.2 mm) in diameter and about 1¼ in. (31.8 mm) in height, the top rim of which is ground smooth and is in a plane essentially parallel with the bottom of the cup.

4.6 *Glass Plate*, with three metal prongs for immersing the soil pat in mercury, as shown in Fig. 1.

4.7 *Graduate*, glass, having a capacity of 25 mL and graduated to 0.2 mL.

4.8 *Balance*, sensitive to 0.1 g.

4.9 *Mercury*, sufficient to fill the glass cup to overflowing.

5. Sampling

5.1 Take a sample weighing about 30 g from the thoroughly mixed portion of the material passing the No. 40 (425-μm) sieve which has been obtained in accordance with Practice D 421.

[1] This method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D 18.03 on Texture, Plasticity, and Density Characteristics of Soils.

Current edition approved Nov. 28, 1983. Published January 1984. Originally issued as D 427 – 35. Last previous edition D 427 – 61 (1974).

[2] *Annual Book of ASTM Standards*, Vol 04.08.

6. Procedure

6.1 Place the sample in the evaporating dish and thoroughly mix with distilled water in an amount sufficient to fill the soil voids completely and to make the soil pasty enough to be readily worked into the shrinkage dish without the inclusion of air bubbles. The amount of water required to furnish friable soils with the desired consistency is equal to or slightly greater than the liquid limit, and the amount necessary to furnish plastic soils with the desired consistency may exceed the liquid limit by as much as 10 %.

6.2 Coat the inside of the shrinkage dish with a thin layer of petroleum jelly or some other heavy grease to prevent the adhesion of the soil to the dish. Place an amount of the wetted soil equal to about one third the volume of the dish in the center of the dish, and cause the soil to flow to the edges by taping the dish on a firm surface cushioned by several layers of blotting paper or similar material. Add an amount of soil approximately equal to the first portion, and tap the dish until the soil is thoroughly compacted and all included air has been brought to the surface. Add more soil and continue the tapping until the dish is completely filled and excess soil stands out about its edge. Strike off the excess soil with a straightedge, and wipe off all soil adhering to the outside of the dish.

6.3 Weigh the dish immediately after it is filled and struck off and record the mass as the mass of dish and wet soil. Allow the soil pat to dry in air until the color of the pat turns from dark to light. Oven-dry the pat to constant mass at 230 ±9°F (110 ±5°C), the mass being recorded as the mass of dish and dry soil. Determine and record the mass of the empty dish. Determine the capacity of the dish in cubic centimetres, which is also the volume of the wet soil pat, by filling the dish to overflowing with mercury, removing the excess by pressing a glass plate firmly over the top of the dish, and measuring by means of a glass graduate the volume of mercury held in the dish (see 6.3.1). Record this volume as the volume of the wet soil pat, V.

6.3.1 **CAUTION:** Mercury is a hazardous substance which can cause serious health effects from prolonged inhalation of the vapor or contact with the skin. The following precautions should be followed whenever mercury is used in the laboratory: (1) Always store mercury in a shatterproof, sealed container, (2) Always work with mercury in a well ventilated area, preferably under a fume hood, (3) Avoid direct contact with mercury liquid; wear rubber gloves if direct contact with mercury is unavoidable, (4) Prevent uncontrolled spills by performing that part of the procedure requiring the use of mercury in a large pan which can act as a catchment should mercury be spilled during the procedure, and (5) Uncontrolled spills must be cleaned up as thoroughly as possible; mercury spill clean-up materials may be necessary and can be obtained from laboratory supply companies.

6.4 Determine the volume of the dry soil pat by removing the pat from the shrinkage dish and immersing it in the glass cup full of mercury in the following manner: Fill the glass cup to overflowing with mercury and remove the excess mercury by pressing the glass plate with the three prongs (Fig. 1) firmly over the top of the cup. Carefully wipe off any mercury that may be adhering to the outside of the cup. Place the cup, filled with mercury, in the evaporating dish and place the soil pat on the surface of the mercury. Carefully force the pat under the mercury by means of the glass plate with the three prongs (Fig. 1) and press the plate firmly over the top of the cup. It is essential that no air be trapped under the soil pat. Measure the volume of the mercury so displaced in the glass graduate and record as the volume of the dry soil pat. V_0.

7. Calculation of Moisture Content

7.1 Calculate the moisture content of the soil at the time it was placed in the dish expressed as a percentage of the dry mass of the soil as follows:

$$w = [(W - W_0)/W_0] \times 100$$

where:

w = moisture content of the soil when placed in the dish,

W = mass of wet soil pat obtained by subtracting the mass of the shrinkage dish from the mass of the dish and wet pat, and

W_0 = mass of dry soil pat obtained by subtracting the mass of the shrinkage dish from the mass of the dish and dry pat.

8. Shrinkage Limit

8.1 The shrinkage limit of a soil is the maximum water content at which a reduction in water content will not cause a decrease in the volume of the soil mass.

8.2 Calculate the shrinkage limit, SL, from the data obtained in the volumetric shrinkage determination, as follows:

$$SL = w - [[(V - V_0)\rho_w/W_0] \times 100]$$

where:

SL = shrinkage limit,
w = moisture content of wet soil, in percentage of the mass of oven-dried soil,
V = volume of wet soil pat, ft^3 (cm^3),
V_0 = volume of dry soil pat, ft^3 (cm^3),
W_0 = mass of oven-dried soil pat, lb (g), and
ρ_w = density of water, 62.4 lb/ft^3 or 1.0 g/cm^3.

8.3 *Optional Method*—When both the specific gravity, G_s, and the shrinkage ratio, R, are known, calculate the shrinkage limit as follows:

$$SL = [(1/R) - (1/G_s)] \times 100$$

9. Shrinkage Ratio

9.1 The shrinkage ratio of a soil is the ratio of a given volume change, expressed as a percentage of the dry volume, to the corresponding change in water content above the shrinkage limit, expressed as a percentage of the mass of oven-dried soil.

9.2 Calculate the shrinkage ratio, R, from the data obtained in the volumetric shrinkage determination by the following equation:

$$R = W_0/V_0 \times \rho_w$$

10. Volumetric Shrinkage

10.1 The volumetric shrinkage of the soil is the decrease in volume, expressed as a percentage of the soil mass when dried, of a soil mass when the water content is reduced from a given percentage to the shrinkage limit.

10.2 The volumetric shrinkage, V_s, shall be calculated from the data obtained in the volumetric shrinkage determination by the following equation:

$$V_s = (w_1 - SL)R$$

where:

w_1 = given percentage of water content,
SL = shrinkage limit, and
R = shrinkage ratio.

11. Linear Shrinkage

11.1 The linear shrinkage of a soil is the decrease in one dimension of a soil mass expressed as a percentage of the original dimension, when the water content is reduced from a given value to the shrinkage limit.

11.2 The linear shrinkage, L_s, shall be obtained by means of the following equation:

$$L_s = 100\ [1 - \sqrt[3]{100/(V_s + 100)}]$$

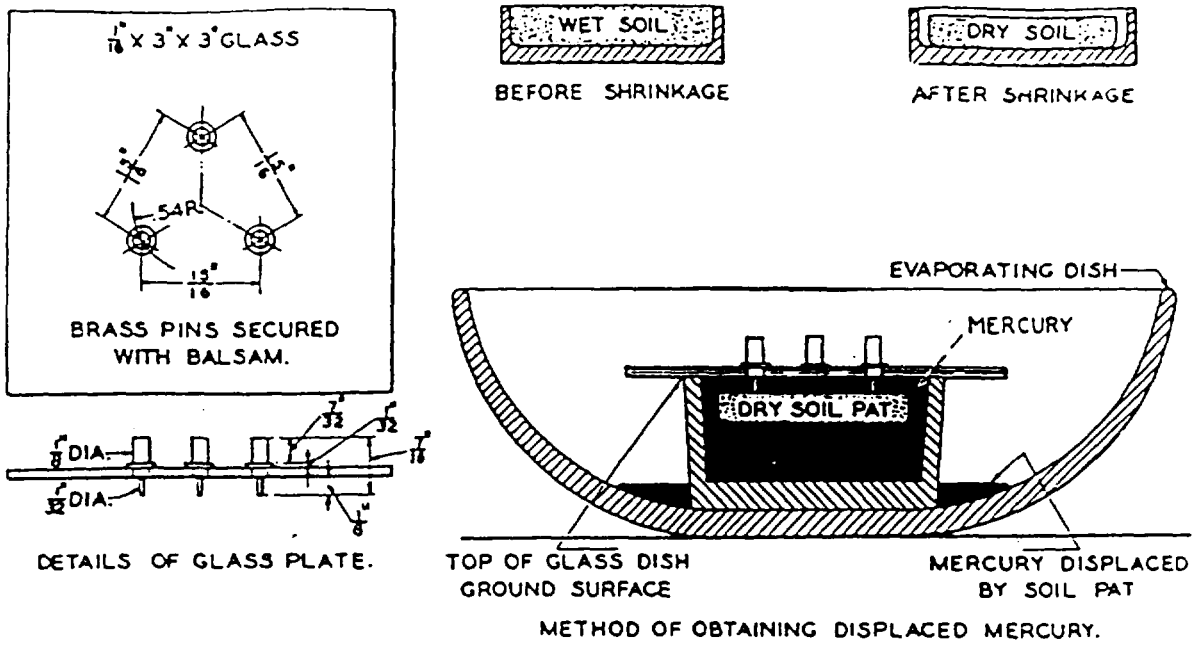
12. Specific Gravity

12.1 The specific gravity of the soil solids, G_s, may be calculated from the data obtained in the volumetric shrinkage test by the following equation:

$$G_s = 1/[(1/R) - (SL/100)]$$

13. Precision and Bias

13.1 Requirements for the precision and bias of this test method have not yet been developed.



Metric Equivalents

in.	1/32	1/16	1/8	7/32	7/16	13/16	3
mm	0.8	1.6	3.2	5.6	11.1	23.8	76.2

FIG. 1 Apparatus for Determining the Volumetric Change of Subgrade Soils

SHRINKAGE LIMIT TEST

Project _____ Job No. _____

Location of Project _____ Boring No. _____ Sample No. _____

Description of Soil _____ Depth of Sample _____

Tested By _____ Date of Testing _____

Wt. of coated dish + wet soil = _____ g

Wt. of coated dish + dry soil = _____ g

Wt. of coated dish = _____ g

Wt. of soil, W_s = _____ g

Wt. of Water, W_w = _____ g

Water content, w_o% = _____ g

Vol. of Wet Soil, V_o = _____ cu cm (Step 5 of procedure: Vol. of shrinkage dish = V_w)

Vol. of Dry Soil, V_f = _____ cu cm (Step 7 of procedure)

Shrinkage limit, $w_s = w_o - \frac{(V_o - V_f)\,\gamma_w}{W_s} \times 100 =$ _____

Shrinkage ratio, $SR = W_s / V_f$ = _____

WARZYN

APPENDIX B-16

GRAIN SIZE (WARZYN)

Designation: D 422 – 63 (Reapproved 1990)$^{\epsilon 1}$

Standard Test Method for Particle-Size Analysis of Soils[1]

This standard is issued under the fixed designation D 422; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

[ε1] NOTE—Section 19 was added editorially in September 1990.

1. Scope

1.1 This test method covers the quantitative determination of the distribution of particle sizes in soils. The distribution of particle sizes larger than 75 μm (retained on the No. 200 sieve) is determined by sieving, while the distribution of particle sizes smaller than 75 μm is determined by a sedimentation process, using a hydrometer to secure the necessary data (Notes 1 and 2).

NOTE 1—Separation may be made on the No. 4 (4.75-mm), No. 40 (425-μm), or No. 200 (75-μm) sieve instead of the No. 10. For whatever sieve used, the size shall be indicated in the report.

NOTE 2—Two types of dispersion devices are provided: (*1*) a high-speed mechanical stirrer, and (*2*) air dispersion. Extensive investigations indicate that air-dispersion devices produce a more positive dispersion of plastic soils below the 20-μm size and appreciably less degradation on all sizes when used with sandy soils. Because of the definite advantages favoring air dispersion, its use is recommended. The results from the two types of devices differ in magnitude, depending upon soil type, leading to marked differences in particle size distribution, especially for sizes finer than 20 μm.

2. Referenced Documents

2.1 *ASTM Standards:*

D 421 Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[3]

E 100 Specification for ASTM Hydrometers[4]

3. Apparatus

3.1 *Balances*—A balance sensitive to 0.01 g for weighing the material passing a No. 10 (2.00-mm) sieve, and a balance sensitive to 0.1 % of the mass of the sample to be weighed for weighing the material retained on a No. 10 sieve.

3.2 *Stirring Apparatus*—Either apparatus A or B may be used.

3.2.1 Apparatus A shall consist of a mechanically operated stirring device in which a suitably mounted electric motor turns a vertical shaft at a speed of not less than 10 000 rpm without load. The shaft shall be equipped with a replaceable stirring paddle made of metal, plastic, or hard rubber, as shown in Fig. 1. The shaft shall be of such length that the stirring paddle will operate not less than ¾ in. (19.0 mm) nor more than 1½ in. (38.1 mm) above the bottom of the dispersion cup. A special dispersion cup conforming to either of the designs shown in Fig. 2 shall be provided to hold the sample while it is being dispersed.

3.2.2 Apparatus B shall consist of an air-jet dispersion cup[5] (Note 3) conforming to the general details shown in Fig. 3 (Notes 4 and 5).

NOTE 3—The amount of air required by an air-jet dispersion cup is of the order of 2 ft^3/min; some small air compressors are not capable of supplying sufficient air to operate a cup.

NOTE 4—Another air-type dispersion device, known as a dispersion tube, developed by Chu and Davidson at Iowa State College, has been shown to give results equivalent to those secured by the air-jet dispersion cups. When it is used, soaking of the sample can be done in the sedimentation cylinder, thus eliminating the need for transferring the slurry. When the air-dispersion tube is used, it shall be so indicated in the report.

NOTE 5—Water may condense in air lines when not in use. This water must be removed, either by using a water trap on the air line, or by blowing the water out of the line before using any of the air for dispersion purposes.

3.3 *Hydrometer*—An ASTM hydrometer, graduated to read in either specific gravity of the suspension or grams per litre of suspension, and conforming to the requirements for hydrometers 151H or 152H in Specifications E 100. Dimensions of both hydrometers are the same, the scale being the only item of difference.

3.4 *Sedimentation Cylinder*—A glass cylinder essentially 18 in. (457 mm) in height and 2½ in. (63.5 mm) in diameter, and marked for a volume of 1000 mL. The inside diameter shall be such that the 1000-mL mark is 36 ± 2 cm from the bottom on the inside.

3.5 *Thermometer*—A thermometer accurate to 1°F (0.5°C).

3.6 *Sieves*—A series of sieves, of square-mesh woven-wire cloth, conforming to the requirements of Specification E 11. A full set of sieves includes the following (Note 6):

[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

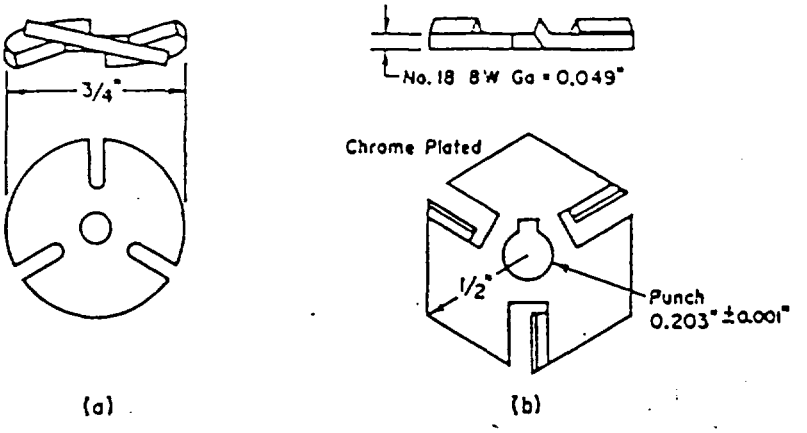
Current edition approved Nov. 21, 1963. Originally published 1935. Replaces D 422 – 62.

[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] *Annual Book of ASTM Standards*, Vol 14.03.

[5] Detailed working drawings for this cup are available at a nominal cost from the American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19103. Order Adjunct No. 12-404220-00.



Metric Equivalents					
in.	0.001	0.049	0.203	½	¾
mm	0.03	1.24	5.16	12.7	19.0

FIG. 1 Detail of Stirring Paddles

3-in. (75-mm)	No. 10 (2.00-mm)
2-in. (50-mm)	No. 20 (850-μm)
1½-in. (37.5-mm)	No. 40 (425-μm)
1-in. (25.0-mm)	No. 60 (250-μm)
¾-in. (19.0-mm)	No. 140 (106-μm)
⅜-in. (9.5-mm)	No. 200 (75-μm)
No. 4 (4.75-mm)	

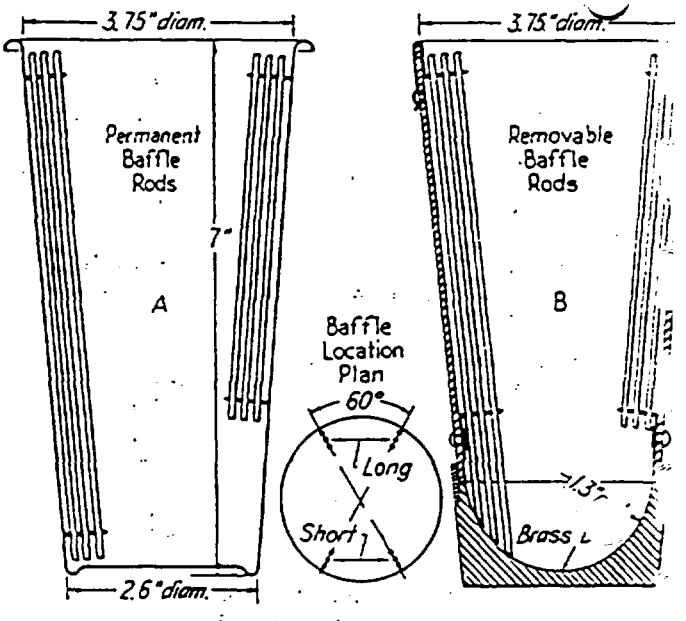
NOTE 6—A set of sieves giving uniform spacing of points for the graph, as required in Section 17, may be used if desired. This set consists of the following sieves:

3-in. (75-mm)	No. 16 (1.18-mm)
1½-in. (37.5-mm)	No. 30 (600-μm)
¾-in. (19.0-mm)	No. 50 (300-μm)
⅜-in. (9.5-mm)	No. 100 (150-μm)
No. 4 (4.75-mm)	No. 200 (75-μm)
No. 8 (2.36-mm)	

3.7 *Water Bath or Constant-Temperature Room*—A water bath or constant-temperature room for maintaining the soil suspension at a constant temperature during the hydrometer analysis. A satisfactory water tank is an insulated tank that maintains the temperature of the suspension at a convenient constant temperature at or near 68°F (20°C). Such a device is illustrated in Fig. 4. In cases where the work is performed in a room at an automatically controlled constant temperature, the water bath is not necessary.

3.8 *Beaker*—A beaker of 250-mL capacity.

3.9 *Timing Device*—A watch or clock with a second hand.



Metric Equivalents			
in.	1.3	2.6	3.75
mm	33	66	95.2

FIG. 2 Dispersion Cups of Apparatus

4. Dispersing Agent

4.1 A solution of sodium hexametaphosphate (sometimes called sodium metaphosphate) shall be used in distilled or demineralized water, at the rate of 40 g of sodium hexametaphosphate/litre of solution (Note 7).

NOTE 7—Solutions of this salt, if acidic, slowly revert or hydrolyze back to the orthophosphate form with a resultant decrease in dispersive action. Solutions should be prepared frequently (at least once a month) or adjusted to pH of 8 or 9 by means of sodium carbonate. Bottles containing solutions should have the date of preparation marked on them.

4.2 All water used shall be either distilled or demineralized water. The water for a hydrometer test shall be brought to the temperature that is expected to prev during the hydrometer test. For example, if the sedimen tion cylinder is to be placed in the water bath, the distilled demineralized water to be used shall be brought to temperature of the controlled water bath; or, if the sedim tation cylinder is used in a room with controlled temper ture, the water for the test shall be at the temperature of room. The basic temperature for the hydrometer test is 6 (20°C). Small variations of temperature do not introdu differences that are of practical significance and do n prevent the use of corrections derived as prescribed.

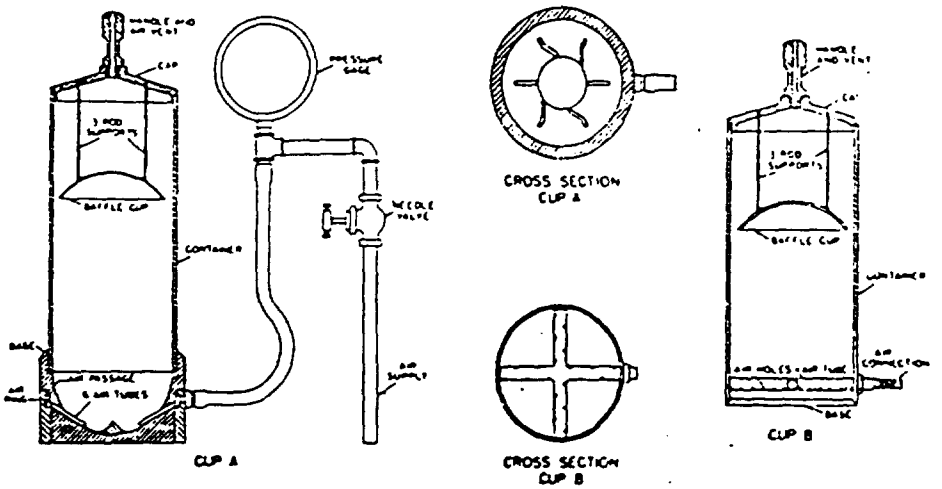


FIG. 3 Air-Jet Dispersion Cups of Apparatus B

5. Test Sample

5.1 Prepare the test sample for mechanical analysis as outlined in Practice D 421. During the preparation procedure the sample is divided into two portions. One portion contains only particles retained on the No. 10 (2.00-mm) sieve while the other portion contains only particles passing the No. 10 sieve. The mass of air-dried soil selected for purpose of tests, as prescribed in Practice D 421, shall be sufficient to yield quantities for mechanical analysis as follows:

5.1.1 The size of the portion retained on the No. 10 sieve shall depend on the maximum size of particle, according to the following schedule:

Nominal Diameter of Largest Particles, in. (mm)	Approximate Minimum Mass of Portion, g
⅜ (9.5)	500
¾ (19.0)	1000
1 (25.4)	2000
1½ (38.1)	3000
2 (50.8)	4000
3 (76.2)	5000

5.1.2 The size of the portion passing the No. 10 sieve shall be approximately 115 g for sandy soils and approximately 65 g for silt and clay soils.

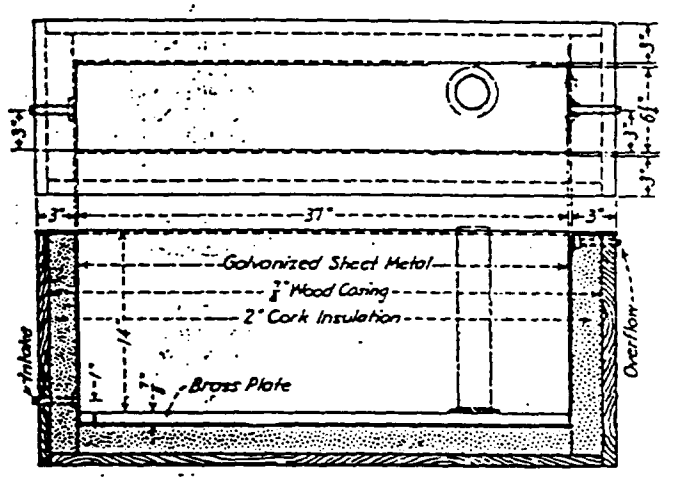
5.2 Provision is made in Section 5 of Practice D 421 for weighing of the air-dry soil selected for purpose of tests, the separation of the soil on the No. 10 sieve by dry-sieving and washing, and the weighing of the washed and dried fraction retained on the No. 10 sieve. From these two masses the percentages retained and passing the No. 10 sieve can be calculated in accordance with 12.1.

NOTE 8—A check on the mass values and the thoroughness of pulverization of the clods may be secured by weighing the portion passing the No. 10 sieve and adding this value to the mass of the washed and oven-dried portion retained on the No. 10 sieve.

SIEVE ANALYSIS OF PORTION RETAINED ON NO. 10 (2.00-mm) SIEVE

6. Procedure

6.1 Separate the portion retained on the No. 10 (2.00-mm) sieve into a series of fractions using the 3-in. (75-mm), 2-in. (50-mm), 1½-in. (37.5-mm), 1-in. (25.0-mm), ¾-in. (19.0-mm), ⅜-in. (9.5-mm), No. 4 (4.75-mm), and No. 10 sieves, or as many as may be needed depending on the sample, or upon the specifications for the material under test.



Metric Equivalents

in.	⅛	1	3	6¼	14	37
mm	22.2	25.4	76.2	158.2	356	940

FIG. 4 Insulated Water Bath

6.2 Conduct the sieving operation by means of a lateral and vertical motion of the sieve, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. In no case turn or manipulate fragments in the sample through the sieve by hand. Continue sieving until not more than 1 mass % of the residue on a sieve passes that sieve during 1 min of sieving. When mechanical sieving is used, test the thoroughness of sieving by using the hand method of sieving as described above.

6.3 Determine the mass of each fraction on a balance conforming to the requirements of 3.1. At the end of weighing, the sum of the masses retained on all the sieves used should equal closely the original mass of the quantity sieved.

HYDROMETER AND SIEVE ANALYSIS OF PORTION PASSING THE NO. 10 (2.00-mm) SIEVE

7. Determination of Composite Correction for Hydrometer Reading

7.1 Equations for percentages of soil remaining in suspension, as given in 14.3, are based on the use of distilled or demineralized water. A dispersing agent is used in the water, however, and the specific gravity of the resulting liquid is appreciably greater than that of distilled or demineralized water.

7.1.1 Both soil hydrometers are calibrated at 68°F (20°C), and variations in temperature from this standard temperature produce inaccuracies in the actual hydrometer readings. The amount of the inaccuracy increases as the variation from the standard temperature increases.

7.1.2 Hydrometers are graduated by the manufacturer to be read at the bottom of the meniscus formed by the liquid on the stem. Since it is not possible to secure readings of soil suspensions at the bottom of the meniscus, readings must be taken at the top and a correction applied.

7.1.3 The net amount of the corrections for the three items enumerated is designated as the composite correction, and may be determined experimentally.

7.2 For convenience, a graph or table of composite corrections for a series of 1° temperature differences for the range of expected test temperatures may be prepared and used as needed. Measurement of the composite corrections may be made at two temperatures spanning the range of expected test temperatures, and corrections for the intermediate temperatures calculated assuming a straight-line relationship between the two observed values.

7.3 Prepare 1000 mL of liquid composed of distilled or demineralized water and dispersing agent in the same proportion as will prevail in the sedimentation (hydrometer) test. Place the liquid in a sedimentation cyclinder and the cylinder in the constant-temperature water bath, set for one of the two temperatures to be used. When the temperature of the liquid becomes constant, insert the hydrometer, and, after a short interval to permit the hydrometer to come to the temperature of the liquid, read the hydrometer at the top of the meniscus formed on the stem. For hydrometer 151H the composite correction is the difference between this reading and one; for hydrometer 152H it is the difference between the reading and zero. Bring the liquid and the hydrometer to the other temperature to be used, and secure the composite correction as before.

8. Hygroscopic Moisture

8.1 When the sample is weighed for the hydrometer test, weigh out an auxiliary portion of from 10 to 15 g in a small metal or glass container, dry the sample to a constant mass in an oven at 230 ± 9°F (110 ± 5°C), and weigh again. Record the masses.

9. Dispersion of Soil Sample

9.1 When the soil is mostly of the clay and silt sizes, weigh out a sample of air-dry soil of approximately 50 g. When the soil is mostly sand the sample should be approximately 100 g.

9.2 Place the sample in the 250-mL beaker and cover with 125 mL of sodium hexametaphosphate solution (40 g/L). Stir until the soil is thoroughly wetted. Allow to soak for at least 16 h.

9.3 At the end of the soaking period, disperse the sample further, using either stirring apparatus A or B. If stirring apparatus A is used, transfer the soil - water slurry from the beaker into the special dispersion cup shown in Fig. 2, washing any residue from the beaker into the cup with distilled or demineralized water (Note 9). Add distilled or demineralized water, if necessary, so that the cup is not more than half full. Stir for a period of 1 min.

NOTE 9—A large size syringe is a convenient device for handling the water in the washing operation. Other devices include the wash-water bottle and a hose with nozzle connected to a pressurized distilled water tank.

9.4 If stirring apparatus B (Fig. 3) is used, remove the dispersion cup cover cap and connect the cup to a compressed air supply by means of a rubber hose. A air gage must be on the line between the cup and the control valve. Open the control valve so that the gage indicates 1 psi (7 kPa) pressure (Note 10). Transfer the soil - water slurry from the beaker to the air-jet dispersion cup by washing with distilled or demineralized water. Add distilled or demineralized water, if necessary, so that the total volume in the cup is 250 mL, no more.

NOTE 10—The initial air pressure of 1 psi is required to prevent the soil - water mixture from entering the air-jet chamber when the mixture is transferred to the dispersion cup.

9.5 Place the cover cap on the cup and open the air control valve until the gage pressure is 20 psi (140 kPa). Disperse the soil according to the following schedule:

Plasticity Index	Dispersion Period, min
Under 5	5
6 to 20	10
Over 20	15

Soils containing large percentages of mica need be dispersed for only 1 min. After the dispersion period, reduce the air pressure to 1 psi preparatory to transfer of soil - water suspension to the sedimentation cylinder.

10. Hydrometer Test

10.1 Immediately after dispersion, transfer the soil - water slurry to the glass sedimentation cylinder, and add distilled or demineralized water until the total volume is 1000 mL.

10.2 Using the palm of the hand over the open end of the cylinder (or a rubber stopper in the open end), turn the cylinder upside down and back for a period of 1 min to complete the agitation of the slurry (Note 11). At the end of 1 min set the cylinder in a convenient location and take hydrometer readings at the following intervals of time (measured from the beginning of sedimentation), or as many as may be needed, depending on the sample or the specification for the material under test: 2, 5, 15, 30, 60, 250, and 1440 min. If the controlled water bath is used, the sedimentation cylinder should be placed in the bath between the 2- and 5-min readings.

NOTE 11—The number of turns during this minute should be approximately 60, counting the turn upside down and back as two.

Any soil remaining in the bottom of the cylinder during the first few turns should be loosened by vigorous shaking of the cylinder while it is in the inverted position.

10.3 When it is desired to take a hydrometer reading, carefully insert the hydrometer about 20 to 25 s before the reading is due to approximately the depth it will have when the reading is taken. As soon as the reading is taken, carefully remove the hydrometer and place it with a spinning motion in a graduate of clean distilled or demineralized water.

NOTE 12—It is important to remove the hydrometer immediately after each reading. Readings shall be taken at the top of the meniscus formed by the suspension around the stem, since it is not possible to secure readings at the bottom of the meniscus.

10.4 After each reading, take the temperature of the suspension by inserting the thermometer into the suspension.

11. Sieve Analysis

11.1 After taking the final hydrometer reading, transfer the suspension to a No. 200 (75-μm) sieve and wash with tap water until the wash water is clear. Transfer the material on the No. 200 sieve to a suitable container, dry in an oven at 230 ± 9°F (110 ± 5°C) and make a sieve analysis of the portion retained, using as many sieves as desired, or required for the material, or upon the specification of the material under test.

CALCULATIONS AND REPORT

12. Sieve Analysis Values for the Portion Coarser than the No. 10 (2.00-mm) Sieve

12.1 Calculate the percentage passing the No. 10 sieve by dividing the mass passing the No. 10 sieve by the mass of soil originally split on the No. 10 sieve, and multiplying the result by 100. To obtain the mass passing the No. 10 sieve, subtract the mass retained on the No. 10 sieve from the original mass.

12.2 To secure the total mass of soil passing the No. 4 (4.75-mm) sieve, add to the mass of the material passing the No. 10 sieve the mass of the fraction passing the No. 4 sieve and retained on the No. 10 sieve. To secure the total mass of soil passing the ⅜-in. (9.5-mm) sieve, add to the total mass of soil passing the No. 4 sieve, the mass of the fraction passing the ⅜-in. sieve and retained on the No. 4 sieve. For the remaining sieves, continue the calculations in the same manner.

12.3 To determine the total percentage passing for each sieve, divide the total mass passing (see 12.2) by the total mass of sample and multiply the result by 100.

13. Hygroscopic Moisture Correction Factor

13.1 The hydroscopic moisture correction factor is the ratio between the mass of the oven-dried sample and the air-dry mass before drying. It is a number less than one, except when there is no hygroscopic moisture.

14. Percentages of Soil in Suspension

14.1 Calculate the oven-dry mass of soil used in the hydrometer analysis by multiplying the air-dry mass by the hygroscopic moisture correction factor.

14.2 Calculate the mass of a total sample represented by the mass of soil used in the hydrometer test, by dividing the oven-dry mass used by the percentage passing the No. 10 (2.00-mm) sieve, and multiplying the result by 100. This value is the weight W in the equation for percentage remaining in suspension.

TABLE 1 Values of Correction Factor, a, for Different Specific Gravities of Soil Particles[A]

Specific Gravity	Correction Factor[A]
2.95	0.94
2.90	0.95
2.85	0.96
2.80	0.97
2.75	0.98
2.70	0.99
2.65	1.00
2.60	1.01
2.55	1.02
2.50	1.03
2.45	1.05

[A] For use in equation for percentage of soil remaining in suspension when using Hydrometer 152H.

14.3 The percentage of soil remaining in suspension at the level at which the hydrometer is measuring the density of the suspension may be calculated as follows (Note 13): For hydrometer 151H:

$$P = [(100\,000/W) \times G/(G - G_1)](R - G_1)$$

NOTE 13—The bracketed portion of the equation for hydrometer 151H is constant for a series of readings and may be calculated first and then multiplied by the portion in the parentheses.

For hydrometer 152H:

$$P = (Ra/W) \times 100$$

where:

a = correction faction to be applied to the reading of hydrometer 152H. (Values shown on the scale are computed using a specific gravity of 2.65. Correction factors are given in Table 1),

P = percentage of soil remaining in suspension at the level at which the hydrometer measures the density of the suspension,

R = hydrometer reading with composite correction applied (Section 7),

W = oven-dry mass of soil in a total test sample represented by mass of soil dispersed (see 14.2), g,

G = specific gravity of the soil particles, and

G_1 = specific gravity of the liquid in which soil particles are suspended. Use numerical value of one in both instances in the equation. In the first instance any possible variation produces no significant effect, and in the second instance, the composite correction for R is based on a value of one for G_1.

15. Diameter of Soil Particles

15.1 The diameter of a particle corresponding to the percentage indicated by a given hydrometer reading shall be calculated according to Stokes' law (Note 14), on the basis that a particle of this diameter was at the surface of the suspension at the beginning of sedimentation and had settled to the level at which the hydrometer is measuring the density of the suspension. According to Stokes' law:

$$D = \sqrt{[30n/980(G - G_1)]} \times L/T$$

where:

D = diameter of particle, mm,

η = coefficient of viscosity of the suspending medium (in this case water) in poises (varies with changes in temperature of the suspending medium),

L = distance from the surface of the suspension to the level at which the density of the suspension is being measured, cm. (For a given hydrometer and sedimentation cylinder, values vary according to the hydrometer readings. This distance is known as effective depth (Table 2)),

T = interval of time from beginning of sedimentation to the taking of the reading, min,

G = specific gravity of soil particles, and

G_l = specific gravity (relative density) of suspending medium (value may be used as 1.000 for all practical purposes).

NOTE 14—Since Stokes' law considers the terminal velocity of a single sphere falling in an infinity of liquid, the sizes calculated represent the diameter of spheres that would fall at the same rate as the soil particles.

15.2 For convenience in calculations the above equation may be written as follows:

$$D = K\sqrt{L/T}$$

where:

K = constant depending on the temperature of the suspension and the specific gravity of the soil particles. Values of K for a range of temperatures and specific gravities are given in Table 3. The value of K does not change for a series of readings constituting a test, while values of L and T do vary.

15.3 Values of D may be computed with sufficient accuracy, using an ordinary 10-in. slide rule.

NOTE 15—The value of L is divided by T using the A- and B-scales, the square root being indicated on the D-scale. Without ascertaining the value of the square root it may be multiplied by K, using either the C- or CI-scale.

16. Sieve Analysis Values for Portion Finer than No. 10 (2.00-mm) Sieve

16.1 Calculation of percentages passing the various sieves used in sieving the portion of the sample from the hydrometer test involves several steps. The first step is to calculate the mass of the fraction that would have been retained on the No. 10 sieve had it not been removed. This mass is equal to the total percentage retained on the No. 10 sieve (100 minus total percentage passing) times the mass of the total sample represented by the mass of soil used (as calculated in 14.2), and the result divided by 100.

16.2 Calculate next the total mass passing the No. 200 sieve. Add together the fractional masses retained on all the sieves, including the No. 10 sieve, and subtract this sum from the mass of the total sample (as calculated in 14.2).

16.3 Calculate next the total masses passing each of the other sieves, in a manner similar to that given in 12.2.

16.4 Calculate last the total percentages passing by dividing the total mass passing (as calculated in 16.3) by the total mass of sample (as calculated in 14.2), and multiply the result by 100.

17. Graph

17.1 When the hydrometer analysis is performed, a graph of the test results shall be made, plotting the diameters of the particles on a logarithmic scale as the abscissa and the percentages smaller than the corresponding diameters to an

TABLE 2 Values of Effective Depth Based on Hydrometer and Sedimentation Cylinder of Specified Sizes[A]

Hydrometer 151H		Hydrometer 152H			
Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm
1.000	16.3	0	16.3	31	11.2
1.001	16.0	1	16.1	32	11.1
1.002	15.8	2	16.0	33	10.9
1.003	15.5	3	15.8	34	10.7
1.004	15.2	4	15.6	35	10.5
1.005	15.0	5	15.5		
1.006	14.7	6	15.3	36	10.4
1.007	14.4	7	15.2	37	10.2
1.008	14.2	8	15.0	38	10.1
1.009	13.9	9	14.8	39	9.9
1.010	13.7	10	14.7	40	9.7
1.011	13.4	11	14.5	41	9.5
1.012	13.1	12	14.3	42	9.4
1.013	12.9	13	14.2	43	9.2
1.014	12.6	14	14.0	44	9.1
1.015	12.3	15	13.8	45	8.9
1.016	12.1	16	13.7	46	
1.017	11.8	17	13.5	47	
1.018	11.5	18	13.3	48	8.4
1.019	11.3	19	13.2	49	8.3
1.020	11.0	20	13.0	50	8.1
1.021	10.7	21	12.9	51	7.9
1.022	10.5	22	12.7	52	7.8
1.023	10.2	23	12.5	53	7.6
1.024	10.0	24	12.4	54	7.4
1.025	9.7	25	12.2	55	7.3
1.026	9.4	26	12.0	56	7.1
1.027	9.2	27	11.9	57	7.0
1.028	8.9	28	11.7	58	6.8
1.029	8.6	29	11.5	59	6.6
1.030	8.4	30	11.4	60	6.5
1.031	8.1				
1.032	7.8				
1.033	7.6				
1.034	7.3				
1.035	7.0				
1.036	6.8				
1.037	6.5				
1.038	6.2				

[A] Values of effective depth are calculated from the equation:

$$L = L_1 + \tfrac{1}{2}\,[L_2 - (V_B/A)]$$

where:

L = effective depth, cm,

L_1 = distance along the stem of the hydrometer from the top of the bulb to the mark for a hydrometer reading, cm,

L_2 = overall length of the hydrometer bulb, cm,

V_B = volume of hydrometer bulb, cm^3, and

A = cross-sectional area of sedimentation cylinder, cm^2

Values used in calculating the values in Table 2 are as follows:

For both hydrometers, 151H and 152H:

L_2 = 14.0 cm

V_B = 67.0 cm^3

A = 27.8 cm^2

For hydrometer 151H:

L_1 = 10.5 cm for a reading of 1.000

= 2.3 cm for a reading of 1.031

For hydrometer 152H:

L_1 = 10.5 cm for a reading of 0 g/litre

= 2.3 cm for a reading of 50 g/litre

TABLE 3 Values of K for Use in Equation for Computing Diameter of Particle in Hydrometer Analysis

Temperature, °C	Specific Gravity of Soil Particles								
	2.45	2.50	2.55	2.60	2.65	2.70	2.75	2.80	2.85
16	0.01510	0.01505	0.01481	0.01457	0.01435	0.01414	0.01394	0.01374	0.01356
17	0.01511	0.01486	0.01462	0.01439	0.01417	0.01396	0.01376	0.01356	0.01338
18	0.01492	0.01467	0.01443	0.01421	0.01399	0.01378	0.01359	0.01339	0.01321
19	0.01474	0.01449	0.01425	0.01403	0.01382	0.01361	0.01342	0.1323	0.01305
20	0.01456	0.01431	0.01408	0.01386	0.01365	0.01344	0.01325	0.01307	0.01289
21	0.01438	0.01414	0.01391	0.01369	0.01348	0.01328	0.01309	0.01291	0.01273
22	0.01421	0.01397	0.01374	0.01353	0.01332	0.01312	0.01294	0.01276	0.01258
23	0.01404	0.01381	0.01358	0.01337	0.01317	0.01297	0.01279	0.01261	0.01243
24	0.01388	0.01365	0.01342	0.01321	0.01301	0.01282	0.01264	0.01246	0.01229
25	0.01372	0.01349	0.01327	0.01306	0.01286	0.01267	0.01249	0.01232	0.01215
26	0.01357	0.01334	0.01312	0.01291	0.01272	0.01253	0.01235	0.01218	0.01201
27	0.01342	0.01319	0.01297	0.01277	0.01258	0.01239	0.01221	0.01204	0.01188
28	0.01327	0.01304	0.01283	0.01264	0.01244	0.01255	0.01208	0.01191	0.01175
29	0.01312	0.01290	0.01269	0.01249	0.01230	0.01212	0.01195	0.01178	0.01162
30	0.01298	0.01276	0.01256	0.01236	0.01217	0.01199	0.01182	0.01165	0.01149

arithmetic scale as the ordinate. When the hydrometer analysis is not made on a portion of the soil, the preparation of the graph is optional, since values may be secured directly from tabulated data.

18. Report

18.1 The report shall include the following:

18.1.1 Maximum size of particles,

18.1.2 Percentage passing (or retained on) each sieve, which may be tabulated or presented by plotting on a graph (Note 16),

18.1.3 Description of sand and gravel particles:

18.1.3.1 Shape—rounded or angular,

18.1.3.2 Hardness—hard and durable, soft, or weathered and friable,

18.1.4 Specific gravity, if unusually high or low,

18.1.5 Any difficulty in dispersing the fraction passing the No. 10 (2.00-mm) sieve, indicating any change in type and amount of dispersing agent, and

18.1.6 The dispersion device used and the length of the dispersion period.

NOTE 16—This tabulation of graph represents the gradation of the sample tested. If particles larger than those contained in the sample were removed before testing, the report shall so state giving the amount and maximum size.

18.2 For materials tested for compliance with definite specifications, the fractions called for in such specifications shall be reported. The fractions smaller than the No. 10 sieve shall be read from the graph.

18.3 For materials for which compliance with definite specifications is not indicated and when the soil is composed almost entirely of particles passing the No. 4 (4.75-mm) sieve, the results read from the graph may be reported as follows:

(1) Gravel, passing 3-in. and retained on No. 4 sieve ..... %
(2) Sand, passing No. 4 sieve and retained on No. 200 sieve ..... %
  (a) Coarse sand, passing No. 4 sieve and retained on No. 10 sieve ..... %
  (b) Medium sand, passing No. 10 sieve and retained on No. 40 sieve ..... %
  (c) Fine sand, passing No. 40 sieve and retained on No. 200 sieve ..... %
(3) Silt size, 0.074 to 0.005 mm ..... %
(4) Clay size, smaller than 0.005 mm ..... %
  Colloids, smaller than 0.001 mm ..... %

18.4 For materials for which compliance with definite specifications is not indicated and when the soil contains material retained on the No. 4 sieve sufficient to require a sieve analysis on that portion, the results may be reported as follows (Note 17):

SIEVE ANALYSIS

Sieve Size	Percentage Passing
3-in.	.....
2-in.	.....
1½-in.	.....
1-in.	.....
¾-in.	.....
⅜-in.	.....
No. 4 (4.75-mm)	.....
No. 10 (2.00-mm)	.....
No. 40 (425-μm)	.....
No. 200 (75-μm)	.....

HYDROMETER ANALYSIS

0.074 mm	.....
0.005 mm	.....
0.001 mm	.....

NOTE 17—No. 8 (2.36-mm) and No. 50 (300-μm) sieves may be substituted for No. 10 and No. 40 sieves.

19. Keywords

19.1 grain-size; hydrometer analysis; hygroscopic moisture; particle-size; sieve analysis

Designation: D 1140 – 54 (Reapproved 1990)ε1

An American National Standard

Standard Test Method for Amount of Material in Soils Finer Than the No. 200 (75-μm) Sieve[1]

This standard is issued under the fixed designation D 1140; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

ε1 NOTE—Editorial changes were made throughout in September 1990.

1. Scope

1.1 This test method covers determination of the total amount of material in soils finer than the No. 200 (75-μm) sieve.

2. Referenced Documents

2.1 *ASTM Standards:*

D 422 Method for Particle-Size Analysis of Soils[2]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[3]

3. Apparatus

3.1 *Sieves*—A nest of two sieves, the lower being a No. 200 (75-μm) sieve and the upper a No. 40 (425-μm) sieve, both conforming to ASTM Specification E 11.

3.2 *Containers*—A pan or vessel of sufficient size to contain the test sample covered with water and to permit vigorous agitation without advertent loss of any part of the sample, and a second pan or container for use in drying the test sample after washing.

4. Test Sample

4.1 The test sample shall be selected from material that has been thoroughly mixed. A representative sample, sufficient to yield not less than the approximate weight of dried material shown in the following table, shall be selected using a sample splitter or by the method of quartering:

Nominal Diameter of Largest Particle, in.	Approximate Minimum Weight of Sample, g
0.0787 (No. 10 sieve) (2.0 mm)	200
0.187 (No. 4 sieve) (4.75 mm)	500
¾ (19.0 mm)	1500
1 (25.0 mm)	2000
1½ or over (37.5 mm)	2500

5. Procedure

5.1 Dry the test sample to a constant weight at a temperature not exceeding 230 ± 9 F (110 ± 5 C) and weigh to the nearest 0.05 percent, or alternatively, weigh the test sample moist and use an auxiliary moisture content sample to determine the moisture content of the sample. The weight of the moisture content sample shall be between 20 and 30 percent of the weight of the test sample. Calculate the oven-dry weight of the test sample from the moist weight and the moisture content.

5.2 Place the test sample in the container, add sufficient clean water to cover it, and allow to soak a minimum of 2 h (preferably overnight).

5.3 Agitate the contents of the container vigorously and pour the wash water immediately over the nested sieves, arranged with the coarser sieve on top. Repeat the process of adding clear water to the container to cover the sample, agitating the contents of the container, and pouring the wash water over the nested sieves until the wash water is clear. When the total sample is small, the entire contents of the soaking container may be transferred to the nested sieves after the first washing and the washing operation completed in accordance with 5.4. The wash water need not be saved.

NOTE 1—The percentage value secured at the end of the test may not be correct (being too low) for soils containing relatively high percentages of the minus 200 fraction. This appears to be due chiefly to inadequate agitation. When it is desired to secure the exact percentage for the minus 200 fraction for such a soil, the portion of the sample passing the No. 40 sieve and retained on the No. 200 sieve secured in the washing operation, shall be transferred to the dispersion cup of the stirring apparatus used in Method D 422. The cup filled half full with water and the contents agitated for 1 min. After this agitation the contents of the cup shall be transferred to the nested sieves and washing continued.

If the stirring apparatus has not been used prior to the drying of the portion of the sample larger than the No. 200 (75-μm) sieve, and it is desired to do so after drying, the dried material shall be separated on the No. 40 (425-μm) sieve; the portion retained shall be saved; and the portion passing shall be placed in the dispersion cup with water and agitated for 1 min with the stirring apparatus as previously described. The contents of the cup shall be transferred to the No. 200 sieve, washed, and dried. The revised total weight retained on the No. 200 sieve shall be secured by combining and weighing the two fractions.

5.4 Transfer the sample to the nested sieves and wash with running water (Note 2). When the sample is larger than can be handled at one time on the nested sieves, wash a portion of the sample and transfer to the container in which it is to be dried.

NOTE 2—Tapping of sieves has been found to expedite the washing operations.

[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity and Density Characteristics of Soils.

Current edition approved Sept. 15, 1954. Originally issued 1950. Replaces D 1140 – 50 T.

[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vols 04.01, 04.02, 04.06, 05.05, and 14.02.

5.5 Dry the washed material retained on the nested sieves in a container to a constant weight at a temperature not exceeding 230 ± 9 F (110 ± 5 C) and dry-sieve it on the nested sieves (Note 3). Weigh the dry material retained on the nested sieves to the nearest 0.05 percent.

NOTE 3—Some material passes the No. 200 (75-μm) sieve on dry sieving that did not pass during the washing operation. When desired, a sieve analysis may be made on the portion of the sample retained on the No. 200 sieve, in accordance with Method D 422.

6. Calculation

6.1 Calculate the results as follows:

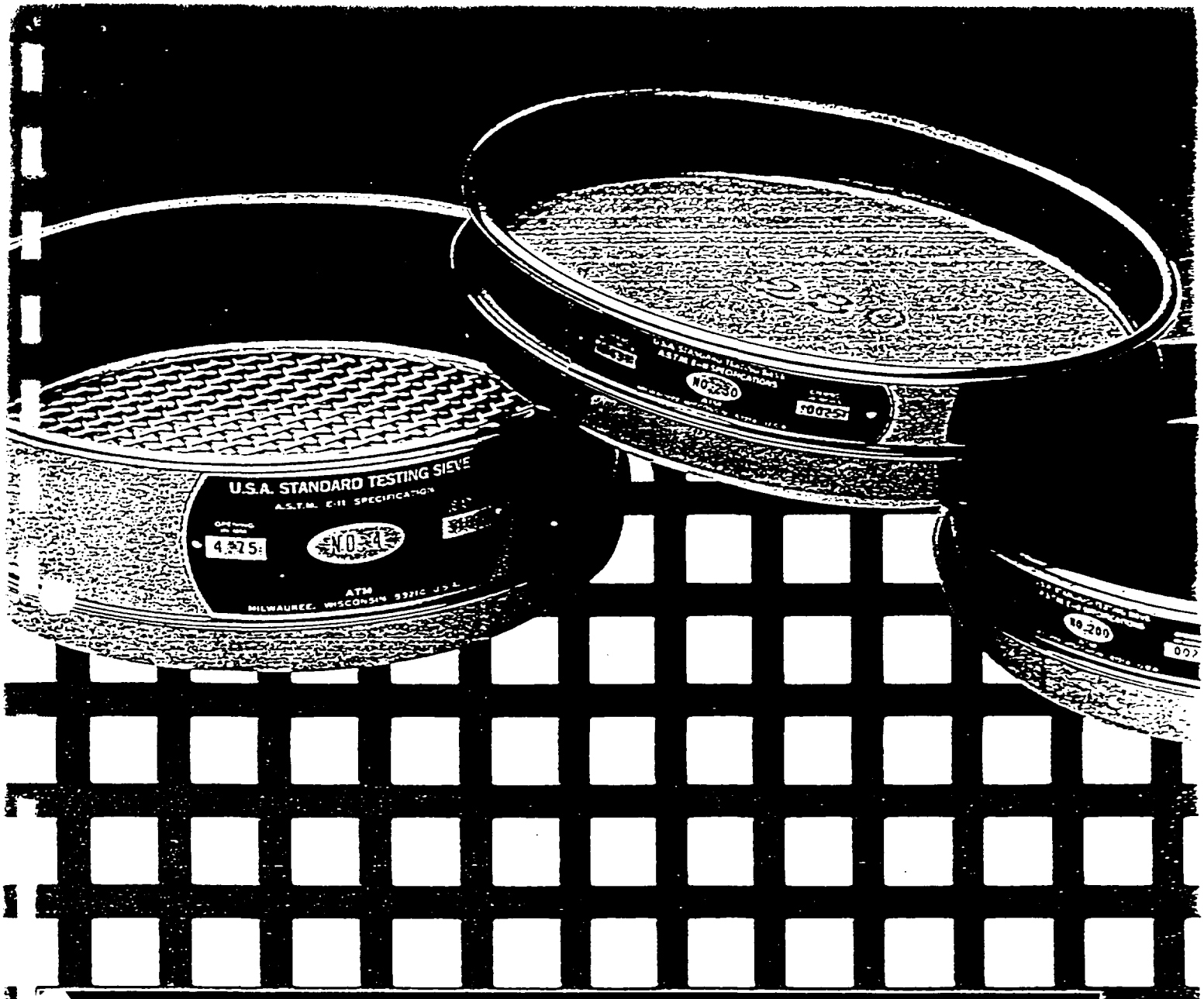
$$P = [(W_o - W_1)/W_o] \times 100$$

where:

P = percentage of material finer than No. 200 (75-μm) sieve,
W_o = weight of original sample on an oven-dry basis, g and
W_1 = oven-dry weight of sample after washing and dry-sieving, g.

7. Keywords

7.1 grain-size; No. 200 sieve; particle-size; sieve analysis



Test Sieving: Principles and Procedures

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CHAPTER 1

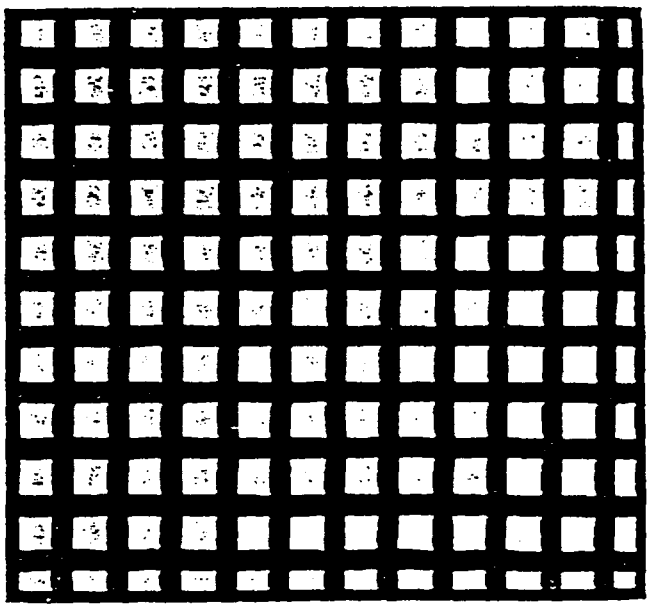
WHAT IS SIEVING?

A simplistic definition of sieving is the removal of fine material from coarse material by means of a meshed or perforated vessel. Professor Terence Allen characterizes sieving as "The aperture of a sieve may be regarded as a series of gauges which reject or pass particles as they are presented to the aperture." (1) This theory was actually in practice during the early Egyptian era as grains were sized with 'sieves' of woven reeds and grasses.

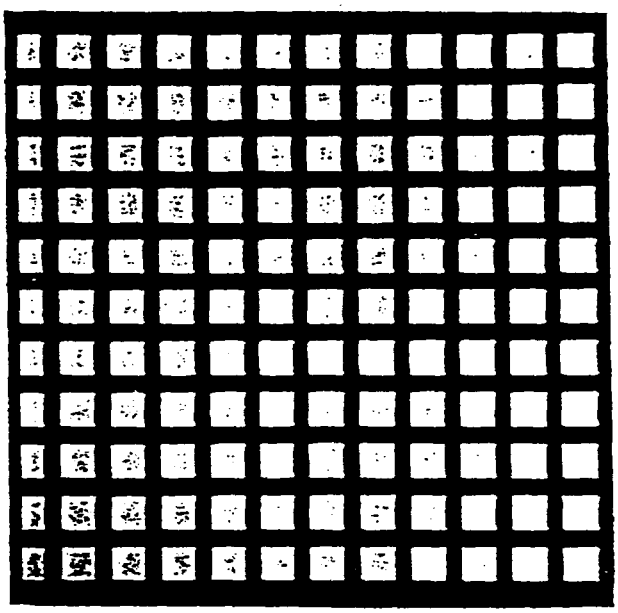
The level of sophistication increased with the rise of the industrial society. As requirements for sized material rose, technology in producing uniform sieving media increased. Woven wire cloth was introduced as an alternative providing greater accuracy and durability. At present, this woven cloth is available in a range of sizes from 5" openings to 20 micrometer openings. All mesh sizes are covered by an array of both national and international standards of tolerance.

The need for particle size anaylsis in the finer size ranges (i.e. 38 micrometers and less) prompted the development of the electrodeposited sieve. These sieves, sometimes called electroformed or micromesh, are currently being produced with openings as fine as 5 micrometers. The mesh openings are extremely uniform in both size and shape and maintain a tolerance of a maximum of 2 micrometer variation.

While the area of sieve analysis has come a long way since the reed sieves of ancient Egypt, few new developments have come along since the 1940's. Professor Kurt Leschonski wrote "Sieve analysis is one of the few methods of particle size analysis which has escaped modernisation (sic)." (2)While the modernization has not come in the actual hardware of sieving, refinements in the application and utilization of existing equipment has proceeded.



WOVEN SIEVE CLOTH
Variations in opening size and shape are common.



ELECTROFORMED SIEVE CLOTH
Electrodeposited material showing uniformity in opening size and shape.

CHAPTER 2

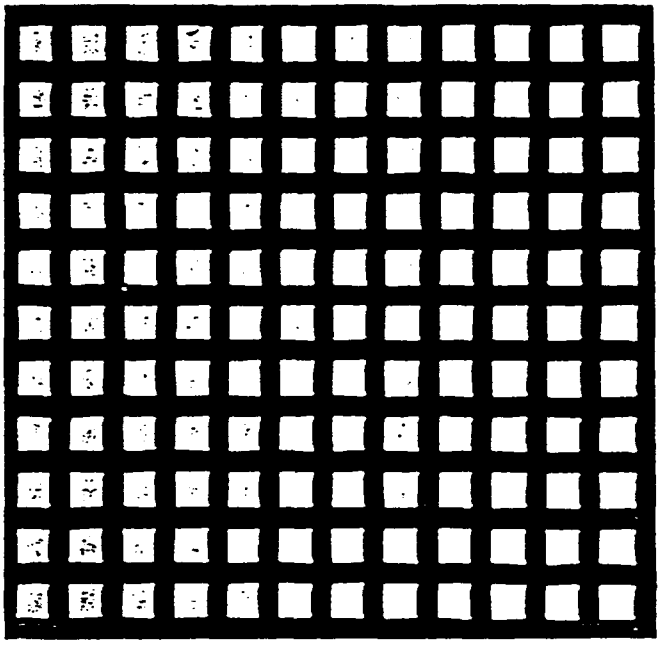
USES, LIMITATIONS AND ADVANTAGES

Harold Heywood wrote "I often refer to sieving as the 'Cinderella' of particle size analysis methods; it does most of the hard work and gets little consideration."(3)

There are numerous reasons for the selection of testing sieves as a first choice in particle size anaylsis work. Leschonski put it "...because of its simplicity — everyone immediately understands the purpose of a stack of sieves and its operation — and its inexpensiveness." (4)Standard sieve analysis is probably the fastest and most widely used quality control procedure in any powder process control industry. Used frequently as a mediating device between the production and sales divisions of a process corporation or between the manufacturer and the customer, test sieve analysis work enjoys the universality of being the best 'quick and dirty' test procedure for rapid particle size distribution data. The outcome of the analysis is easily calculated and interpreted for comparison between laboratories. Start-up cost to institute a basic sieving quality control program is minimal, and operators of most levels of training are capable of performing a successful sieve analysis. With these factors in mind, it is easy to see why testing sieves are as ubiquitous as they are in industry. Materials from crushed ore chunks of over 4½" in diameter to slurried alumina and porcelain powders of less than 20 micrometers are all analyzed with test sieves on a regular basis.

Whether hand or machine sieving, wet or dry preparations, analysis or production work, testing sieves have found a niche in the quality control laboratory. Given this overall acceptance of test sieves as a viable analytical device and the widespread presence of the sieve in laboratories in all industries, any shortcomings of such an analysis device would be magnified. For all of the advantages available to the test sieve user, limitations must be recognized and accounted for in data presentation and analysis.

Test sieves are individuals. Being fabricated of a woven mesh material, variations in the weave are common. The chances of locating two sieves of identical distribution of opening sizes are extremely remote. Because of these variations, reproducibility of test results between sieves is adversely affected. The stringent standards imposed by ASTM, ISO or other regulating bodies have built tolerance factors which allow for the variations in the weave while striving to maintain a level of uniformity in 'test grade' sieve cloth. (See Table 1.)



CLOTH WITH WIDE MESH VARIATIONS

Alternating areas of narrow and wide mesh openings can significantly change sieve analysis results.

With this distribution of opening sizes present, some smaller than the nominal and some larger, the time interval of the sieve analysis becomes extremely important. If, for example, a sieve has several openings far above the tolerance for the particular mesh size, and the test is run for 30 minutes, the probability of larger-than-nominal particles finding those oversize openings is much greater than if the test was run for only 15 minutes. Similarly, if the sample of powder contains a large percentage of elongated or needlelike particles, the longer the test interval, the greater the likelihood that the elongated particles will orient themselves 'on end' and pass through the openings. If the sieve cloth has a wide range of opening sizes, the sieving of such a material has a compounded error.

Another factor which must be carefully analyzed is the reaction of the material to ambient conditions. The most accurate test sieve available would be of

USES, LIMITATIONS AND ADVANTAGES (cont.)

minimal use if the relative humidity in the test lab was 99%. Likewise, extremely dry conditions can cause fine powders to adhere to the sieve parts and each other with strong electrostatic charges. Other types of sieving problems will be discussed in the glossary section.

To minimize the error unavoidably introduced by the wire cloth weavers, steps must be taken at every step of fabrication that assure the uniformity of the woven mesh as well as the compliance with the applicable standards. Both the weaver and the test sieve manfacturer must keep up a constant monitoring program of actual opening sizes of the wire cloth as well as the uniformity of those openings. The loss to the manufacturers in rejected sieve cloth is a gain to the end-user in uniformity and compliance.

COMPARATOR

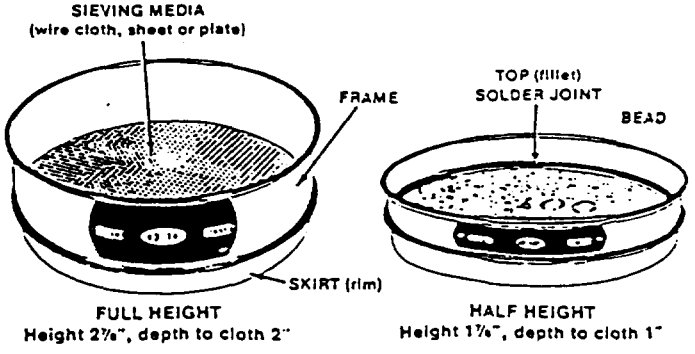
Profile projector specially designed and built for wire cloth and sieve inspection.

CHAPTER 3

WORKING GLOSSARY OF SIEVING TERMS

Sieving terminology is frequently used and abused in writing up specifications for materials. Listed below are some of the most frequently used terms and a general discussion of their meaning:

Agglomerate: natural tendency of materials to clump or ball together. This condition is very common in materials with high fat or oil content or those with fibrous or extremely irregular topography.



Blinding: plugging of the screen openings with particles either exactly the same size as the sieve opening or by fine particles which build up on the meshes and eventually close off the openings. Frequently referred to as pegging. (Photo Page 4)

Cover: stamped or spun lid which tightly covers the top of a sieve to prevent the loss of the material sample during sifting.

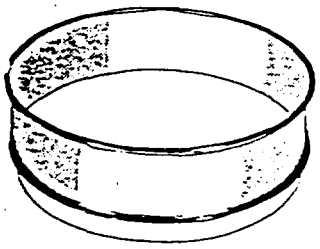
Electrostatic charges: accumulation of electrical charges on the particles and sieve parts causing clinging, agglomeration or blinding. This condition is frequently seen in hydrocarbon based materials, plastics, reactive metals, paint pigments and powders with a large fraction below 20 micrometers.

Extended rim pan: a sieving pan with a skirt designed to nest within a sieve stack, allowing multiple tests to be performed simultaneously. Frequently called a nesting pan or spacer.

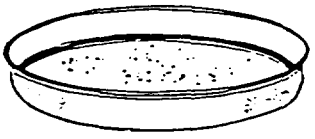
WORKING GLOSSARY OF SIEVING TERMS (cont.)

COVER WITH LIFTING RING

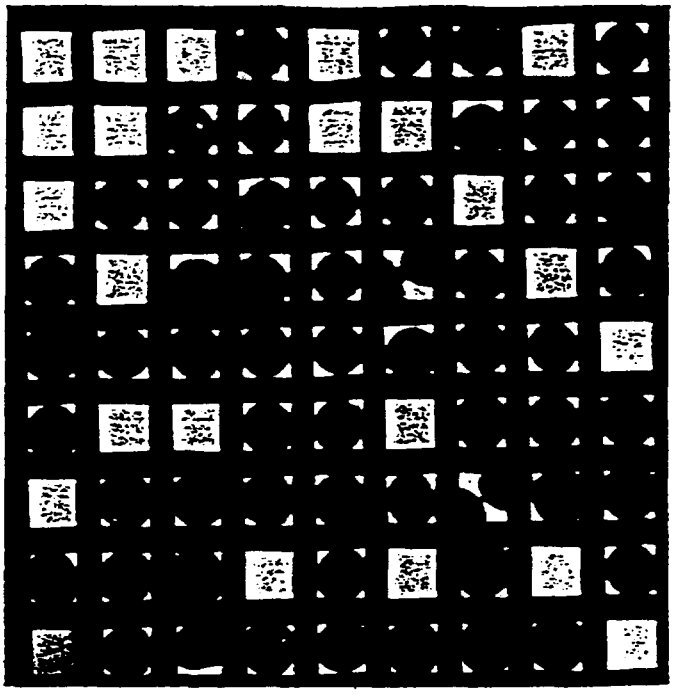
COVER WITHOUT LIFTING RING



EXTENDED RIM PAN
(Spacer)



PAN
(Receiver)



BLINDED SIEVE
Spherical and near-size particles can blind or peg in the sieve openings.

Flow additive: powdered substance added to the sample to reduce agglomeration, neutralize static charges and improve the flow characteristics of the sample. Common additives are fine silica, activated charcoal, talc, and other commercially produced synthetic substances. Generally, the additive is prescreened to a known average particle size, blended with the sample (approximately 1% additive by weight) and then screened.

Frame: rigid sidewall used to form body of the testing sieve. Common depths are 2" (full height) and 1" (half height). Special application sieves of other depths are also in use.

Mesh: screening medium with openings of uniform size and shape fabricated of woven, punched or electrodeposited material.

Pan: stamped or spun receiver of materials passing through the finest sieve.

Skirt: section of test sieve below the sieve mesh which allows for mating or nesting of the sieves in a test stack.

Support mesh: coarse sieve cloth mounted under fine sieve cloth in a test sieve to provide extra strength. This is widely used in wet sieving operations to protect the fragile fine sieve cloth. Frequently called backing cloth or rolled backing cloth.

Test Sieve: screening medium (mesh) with openings of uniform size and shape mounted on a rigid frame, usually for laboratory testing or small scale production applications. The frames can be made of various materials, the most common of which are brass and stainless steel in a cylindrical configuration, having a diameter of 3", 5", 6", 8", 10", 12" or larger.

Wet sieving: the separation of fines from the coarse portion of a sample while suspended in an aqueous solution introduced to a testing sieve. The liquid medium is used to negate static charges, break down agglomerates and lubricate near-size particles. After the fines have been washed through the sieve, the residue is oven-dried and reweighed.

CHAPTER 4

SIEVE SPECIFICATIONS — Domestic and International

The U.S. Sieve Series is a metric system based series first suggested by the American Society of Testing and Materials in 1913. The opening sizes in this sieve series are in the ratio of the fourth root of two. This numerical relationship was first suggested by Professor P.R. Rittinger, a German researcher, in 1867.

In the fourth root of two series, every opening size is 1.189 times the opening size of the next smaller sieve. This relationship continues into sieve opening area measurement. The U.S. Sieve Series provides that the area of each sieve opening size is 1½ times the area of the preceding sieve size.

By using every other sieve in this number series, the relationship becomes based on the square root of two (1.414), with the area of the opening being twice that of the preceding sieve size. Thus, by skipping two sizes, you create an area ratio of 3 to 1, or by skipping three sizes, you create a ratio of 4 to 1.

When selecting sieves from this series, any number of sieves can be used for an analysis. Care must be taken in selecting every sieve between two points, every other sieve, every fourth sieve, etc., to keep within the mathematical progression of the series.

After World War II, the International Standards Organization (ISO) was formed in an attempt to establish world standards. Though the U.S. Sieve Series had proven to be effective and was in use throughout the world, members of the ISO would not accept the U.S. Sieve Series as a world standard. Rather, they chose to adopt the Preferred Number Series based on the roots of ten. The Preferred Number Series was suggested by Charles Renard of France in 1879. His system is based on the tenth, twentieth and fortieth roots of ten (designated R-10, R-20 and R-40). See Table 2.

Compromise was reached between the ISO and the proponents of the U.S. Sieve Series when it was discovered that every third value in the R-40/3 table is in a step ratio of 1.885, sufficiently close to the fourth root of two (1.1892) used by the U.S. Sieve Series. In 1970, slight adjustments were made in the U.S. Sieve Series to align the series perfectly with the ISO specifications.

Copies of these tables of specifications can be found in Table 3.

CHAPTER 5

SIEVE CALIBRATION PROCEDURES

Quantifying and accounting for variations in test sieve results have become two of the most important topics in particle technology today. Once again, the ubiquitous nature of stacks of test sieves in powder labs around the world has contributed to scope of the dilemma in sieve standardization and calibration. Kaye states "The inaccuracies and the uncertainties of characterization by sieve fractionation arise from the experimental problems of determining the sieve residues and from the nonideal nature of the sieving surfaces." Further, "The presence of a range of aperture sizes in any real sieving surface is a source of error in sieve based characterization studies since the theoretical or nominal size of the sieve is taken to be the boundary limit for the sieve residue." (5)

Not only is the test sieve user plagued with variations in the weave of the cloth, but confronted with the effects of particle shape on sieving results. Nearly 50 years ago, A.M. Gaudin wrote "Powders with identical size distributions, densities and chemical composition may behave quite differently as a result of variations in particle shape between samples. For example, powders consisting solely of spherical particles are likely to have good flow properties, while powders containing needlelike particles will not." Further, "In addition, it is impossible to isolate the concepts of particle size

SIEVE CALIBRATION PROCEDURES (cont.)

and shape, since the method of size measurement will influence the particle size which is determined." [6]

Numerous approaches have been tried to compensate for the effects of variations in wire cloth and particle shape. The methods have fallen into 3 basic categories: 1) inspection of the mesh to determine opening size, 2) material testing of the sieves to determine if sieves fall within performance specifications, and 3) a combination of methods 1 and 2, assuring compliance with both opening size and performance specifications.

Probably the most elementary of the inspection methods is the use of the etched glass slide. This procedure relies on what is referred to as the 'Moire Effect' which compares the number of meshes per inch in the wire cloth sample to the number of lines per inch etched on the glass slide. By microscopically measuring the wire diameters, a rough estimate of the opening size can be approximated. One major shortcoming of this procedure is the assumption that all wire diameters within the sample are the same. A slight variation in wire diameter can translate to a significant change in opening size.

An alternative to this measurement approach is the use of a high-powered optical comparator or profile projector. In this method, powerful light sources illuminate the mesh from both above and below and project the image onto a glass screen. Calibrated micrometer stages move the mesh sample in relation to a reference point allowing measurements with accuracy of 1 micrometer to be made on both the opening and wire diameter. The results are displayed on a numerical readout. The broad field of view of the comparator allows for a scan of a large number of sieve openings, facilitating a more comprehensive picture of the nature of the sieve cloth.

In material testing of sieves, powder samples are run on subject sieves and the residue calculated. These values are then compared with other sieves in selecting what some refer to as 'matched' sieves. There are a number of shortcomings in this procedure also. The first and foremost problem encountered is that of compliance. Conceivably, it is possible to find hundreds of sieves that will provide the same performance data when tested with a reference material and still not meet ASTM standards. While the sieves perform comparably, the fact that they do not meet the basic criteria of ASTM specifications should remove them from use as a U.S. Standard sieve. Another problem encountered with material matching is the use of reference samples which are different in shape, size or density than the users' products. For example, a manufacturer of spherical steel shot would yield significantly different results on a sieve that had been matched with an angular ground silica material. In this case, both shape and density are considerably different. The key to proper matching is the use of the user's own product or a material which approximates the product most closely.

The final approach is a combination of the first two methods. First, the sieve is checked optically for compliance with all applicable standards. Openings and wire diameters are physically measured, not averaged. After the sieve opening distribution has been characterized and evaluated, actual material testing can begin. During the material testing, samples of the user's own product are used for the standardization procedure. All tests are run for repeatability and the variation between test results calculated. This procedure yields a testing sieve with known values in the two most essential parameters — compliance with specifications and performance in an 'in vivo' setting.

An alternative that has been used with some success is the use of correction factors between sieves. Once a 'master set' of sieves has been established, a reference sample is tested on the stack. The values are calculated and retained. As new sieves are purchased, the original reference sample is tested on the new set and the values calculated. Any variations between the sieve stacks can be compensated for with correction factors or multipliers. For example, a sieve in stack 3 may retain more or less than the comparable sieve in the master set. A multiplier of magnitude greater than or less than 1 is necessary to calculate the comparable retention value on that sieve when compared to the master set. In this way, every sieve in use can be compared to the master set to standardize sieving results. Whatever method you use, it is essential that your starting point is grounded on the firm foundation of ASTM specifications. The compliance is necessary to assure uniformity between and within industries.

CHAPTER 6

PERFORMING THE SIEVE ANALYSIS

In obtaining meaningful sieve analysis data, three major steps must take place. The first step is the preparation of the sample material, the second step is the performance of the actual sieving technique and the final step is the computation, presentation and analysis of the data.

Sample extraction and preparation is the most commonly overlooked variable in sieve standardization programs. Testing bias can be added at many places along the progression from material production to data analysis. The way the samples are extracted from the original bulk volume varies with the way the materials are produced or stored. The ideal sampling method is one which produces the most representative sample with the least amount of material required.

The following paragraphs were first published in the ASTM technical publication STP 447A. The collaborative efforts of the authors have produced a section on sampling technique which cannot be improved upon. (7)

Sampling from a chute or belt

Good accuracy in sampling is obtained where material is flowing from a chute or belt conveyor. The ideal place to take the sample is just where the material drops from the chute or belt. When taking the sample, if the stream is small enough, use a pail or other suitable receptacle which can be swung completely across the flowing stream in a brief interval of time and with a uniform movement. Under no circumstances should the sampling receptacle be allowed to overflow, because the overflow would tend to reject a higher proportion of the larger particles that exist in a representative sample. Mechanical sampling devices are available for selecting samples automatically from a stream at uniform spaced intervals of time.

Sampling from carload shipments of course bulk material

For coarse materials, such as crushed stone and gravel, shipped in railroad cars, a recommended method is to dig three or more trenches at least 1 foot (30.48 cm) deep and approximately 1 foot (30.48 cm) wide at the bottom. Equal portions are taken at seven equally spaced points along the bottom of the trench by pushing a shovel downward into the material and not by scraping horizontally. Samples from trucks, barges, or boats should be taken in the same manner as from railroad cars, except that the number of trenches should be adjusted to size of the transportation unit and tonnage involved.

Sampling from carload shipments of fine bulk materials

One established method for sampling a carload of bulk granular material is to take eight equal samples, (approximately 700 to 1000 grams each) from the bottom of a 1 foot (30.48 cm) conical excavation. Samples should be suitably spaced to represent the length and width of the car and then combined into a single gross sample.

Sampling bulk shipments of fine material with a sampling tube

An alternate and simpler method of sampling a carload, or other bulk quantity of fine or granular material is by use of a sampling tube which, for this purpose, should be 1½ inches (38.1 mm) by approximately 6 feet (1.829 m). Five or six insertions of the tube will produce approximately, a 2 pound (907-g) sample.

Sampling from a carload of bagged material

One method of sampling a carload of material shipped in bags is to select, at random, a number of bags equal to the cube root of the total number of bags in the car and to take suitable portions (800 to 1000 grams for minus 6 mm material) from each of the selected bags for a combined gross sample.

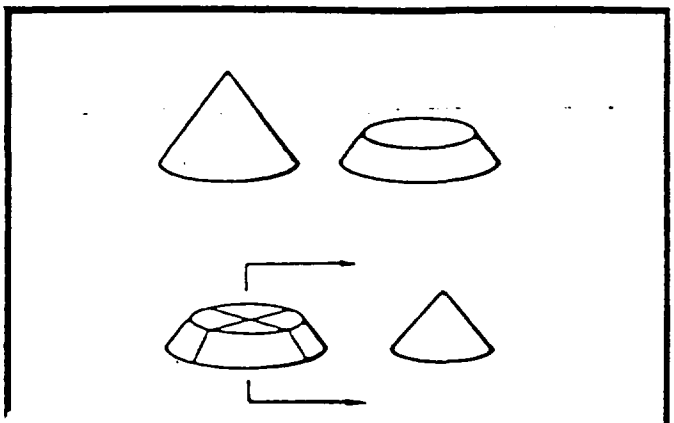
Sampling from a pile

In sampling from a pile, particularly material like crushed stone or coal containing large particles, it is extremely difficult to secure samples that are truly representative. At the apex of a conical pile, the proportion of fines will be greater, while at the base, the percentage of coarse particles will be greater. Therefore, neither location will be representative of the whole. In a shoveling process, every fifth or tenth shovel, etc., should be taken depending on the amount of the sample desired. The sample should consist of small quantities taken at random from as many parts of the pile as are accessible and taken in a manner that the composite will have the same grading as the larger amount.

Reduction of gross sample to test size for sieve analysis

After the gross sample has been properly taken, the next step is to reduce it to a suitable size for the sieve analysis test without impairing in any way the particle size distribution

PERFORMING THE SIEVE ANALYSIS (cont.)



CONING AND QUARTERING TECHNIQUE

characteristics of the original sample. This phase of the operation should follow the applicable procedures described in the succeeding sections, and should be performed with as much care as was used in the collection of the gross sample and in making the sieve test.

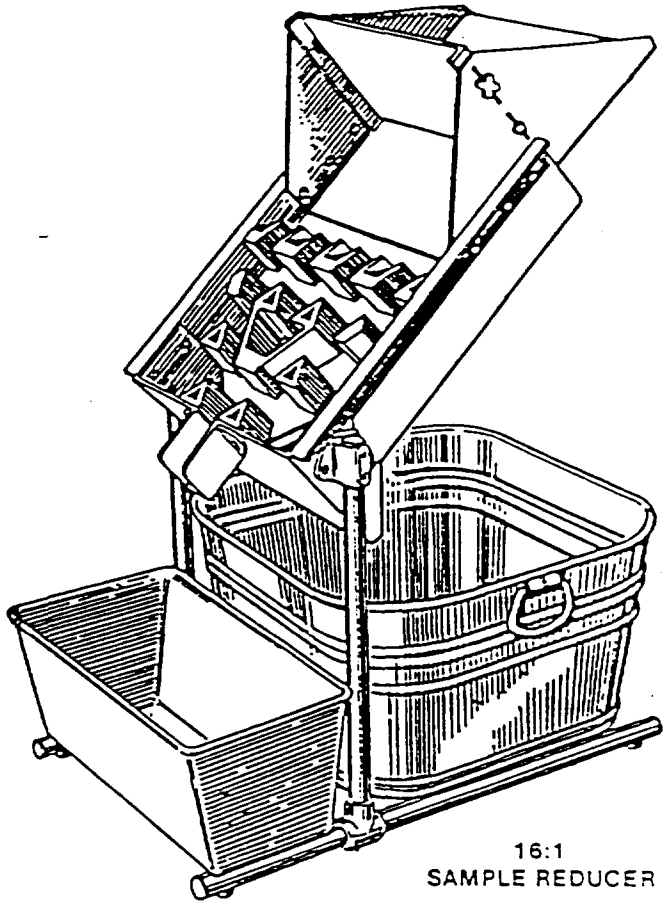
Coning and quartering

Pile the gross sample in a cone, place each shovelful at the apex of the cone, and allow it to run down equally in all directions. This will mix the sample. Then spread the sample in a circle and walk around the pile, gradually flattening the circle with a shovel until the material is spread to a uniform thickness.

Mark the flat pile into quarters, and reject two opposite quarters. Mix again into a conical pile, taking alternate shovelfuls from the two quarters saved. Continue the process of piling, flattening, and rejecting two quarters until the sample is reduced to the required size.

Sample splitters and reducers

Gross samples, if not too large, may be reduced to test sample size by one or more passes through a sample splitter or Jones type riffler, which will divide a sample in half while maintaining the particle size distribution of the original sample. By repeated passes, the sample can be split into quarters, eighths, etc., until the size of the sample desired is obtained. For larger gross samples, sample reducers are available which will select a representative 16 part with a single pass. By just two passes through such a unit, a representative 1 pound sample can be obtained from an original 256 pounds. Three passes will give a 1 pound sample from two tons of material. Always make sure that the passages in the splitter or reducer are at least three times the size of the largest particle in the sample. Do not attempt to arrive at exactly the amount of material specified for the test. If a 50 gram sample is desired, arrive as near to this amount as practicable, because it will make no difference in the test percentage results whether the sample is slightly larger or smaller. In attempting to arrive at an exact weight, the tendency is to discriminate by the removal of sizes which are not representative of the whole, thus destroying the representative quality of the sample.



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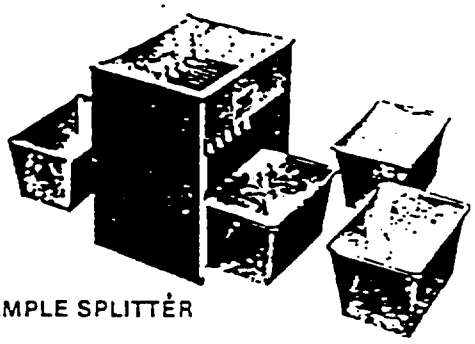
SAMPLE REDUCER



SAMPLE SPLITTER

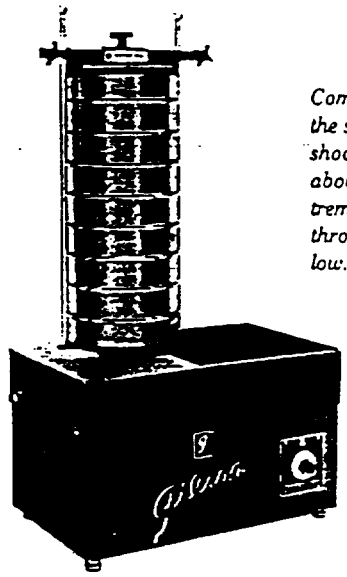
PERFORMING THE SIEVE ANALYSIS (cont.)

Size of Sample in the Test

There is a natural tendency, although incorrect, to use too large a sample in the test. In most cases, the smaller the sample the more accurate the analysis. Testing sieves are the same as a go or no go gauge and too large a sample does not permit all the particles to present themselves to the screen surface.

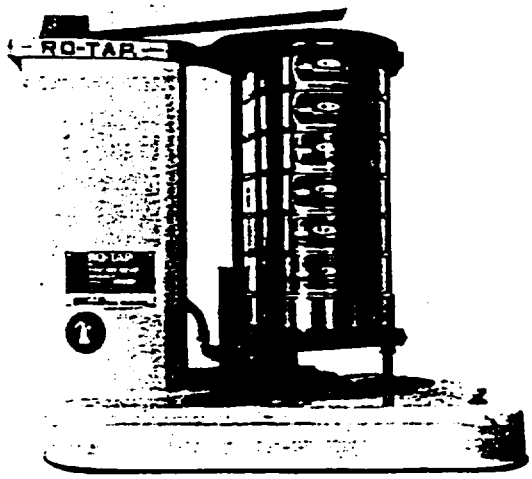
Generally speaking a 25 to 100 gram sample should be used, however, if it is necessary to establish the correct sample size follow the following procedure. With a sample splitter accurately split, select samples of various weights such as 25, 50, 100 and 200 grams. Run these various sample sizes on a selected nest of sieves for a period of five minutes preferably on a mechanical sieve shaker. If the test with the 100 gram sample shows approximately the same percentage passing the finest sieve as the 50 gram sample, whereas the 200 gram sample shows a lower percentage, this would indicate that the 200 gram sample is too large and the 100 gram sample would be satisfactory. Then run the 100 gram sample on the same set of sieves for the same sieving time to see if you get repetitive results. Once the correct size sample has been determined use this on all sieve tests.

A useful table of recommended sample sizes for tests with 200 mm or 8" diameter sieves is Table 4. Note that the table gives sample sizes listed by volume. Recommended sample weights in grams can be determined by multiplying the values in Column 3 and 4 by the bulk density (grams per cubic centimeter) of the material to be tested rounded out within a reasonable tolerance. If the actual bulk density of a certain material is not known, the typical density factor for the most nearly similar material listed in Table 5, may be used.



SIEVE SHAKER

Combined circular motion of the sieve stack with alternating shock from both below and above makes this shaker extremely effective from #4 mesh through #200 mesh and below.



RO-TAP SIEVE SHAKER

Combined circular motion of the sieve stack with shock from above the sieve stack mixes and redistributes powder on the sieves. Applicable over the ASTM E-11 sieve range.

PERFORMING THE SIEVE ANALYSIS (cont.)

SONIC SIFTER

A viable alternative for fine powder sieving using a unique oscillating air column. The effective size range is 5660 µm (3.5 mesh) through 5 µm using 3" diameter acrylic frame sieves. This method has the advantages of high accuracy with a low test time, while showing no signs of particle attrition or screen wear.

To perform the actual sieve analysis, screens should be chosen in a sequence as described earlier. Use either every sieve, every other sieve, every third sieve, etc. between the desired size parameters. The use of screens in this sequential order will allow for better data presentation and a more meaningful analysis of the test results. Care should also be taken in selecting the proper sieves to avoid overloading any sieve with an especially large material peak. For example, a specification may require 96% of the sample be retained above a #50 mesh sieve. The proper way to perform an analysis of this nature is to use 'relief screens', that is, sieves in the 30, 35, 40 and 45 mesh ranges to remove some of the burden from the critical cut point of 50 mesh. If the relief screens are not used, particles of exactly 50 mesh size or slightly larger will be driven through by the mass of material resting above them. The screen cut point would be inaccurate and sample would not meet the specifications for the test.

The selected sieves should be assembled with the coarsest sieve at the top of the stack, and the balance of the stack in increasing magnitude of fineness (increasing sieve numbers). The stack should be finished off with a cover on the top sieve and a pan below the finest sieve. At this point, the sieve stack is either shaken and rapped by hand, or mounted in a sieve shaker with a motorized or electrostatic drive mechanism.

While many applications still use the hand-shaken method for sieving, motor driven shakers have proven to be much more consistent, not having to account for differences in operators. In the case of powder analysis below the 100 mesh range, the sieve shaker should be equipped with a device to impart a shock wave to the sieve stack at regular intervals. This hammer or rapping device is necessary to reorient the particles on the screen and impart some shear forces to near-size particles blocking the sieve openings.

The duration of the sieving interval is usually regulated by industry standards, or by in-house control specifications. Commonly, 10, 15 or 20 minute tests are used as arbitrary sieving intervals. To determine the best interval for a new material, or to double check the accuracy of existing specifications, the following procedure can be used. Select the desired sieves for the analysis. Weigh up a sample of the material to be tested and introduce it to the completed sieve stack. Shake the sieve stack for a period of 5 minutes. Weigh the residue in the pan and calculate the percentage in relation to the starting weight. Reassemble the stack and shake for one additional minute. Repeat the weigh-up procedure and calculate the percentage. If the percentage of fines increased more than 1% between 5 minutes and 6 minutes, reassemble the stack and shake for an additional minute. The data can be plotted as percentage throughput vs. time for each data point you calculate. When the change in the percentage of fines passing in the 1 minute period drops below 1%, the test can be considered complete. Record the total testing time for subsequent analysis.

Another type of sieve analysis is the wet sieve test. In this method, the sample is weighed and then washed through the finest sieve in the stack with water, water with a wetting agent or some other compatible solvent. After thoroughly washing the fines from the raw sample, the residue is dried either over a hot plate or in an oven. Care must be taken to keep the temperature of the sieve below 300°F (149°C) to avoid loosening of the sieve cloth or failure of the solder joint. After drying, the residue is then sieved normally on the balance of the sieve stack. The loss in weight not accounted for on the coarse screens is assumed to be fines.

Wet sieve analysis is especially helpful when working with naturally agglomerated materials, ultrafine powders with severe static changes, and in samples where fine particles tend to cling to the coarse fractions in the blend. The disadvantages associated with wet sieving are primarily the time period required to perform the analysis due to drying time and the possible damage to the sieve mesh by overloading. A common practice with wet sieving operations is brushing or forcing the

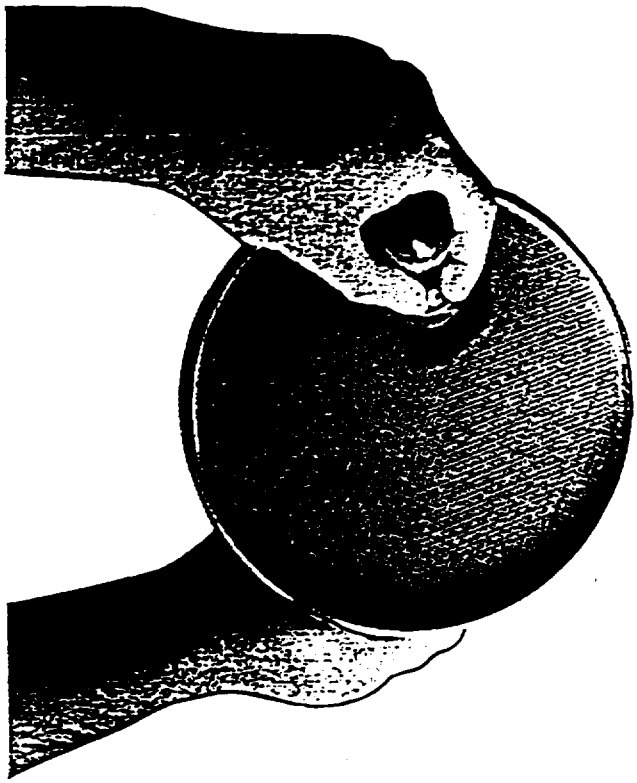
PERFORMING THE SIEVE ANALYSIS (cont.)

sample through the mesh while the liquid medium is directed on the sieve. This pressure can distort the sieve openings or tear the mesh at the solder joint through stress.

Once the sieving interval is complete, whether dry or wet sieving is used, the residue on each sieve is removed by pouring the residue into a suitable weighing vessel. To remove material wedged in the sieving openings, the sieve is inverted over a sheet of paper or suitable collector and the underside of the wire cloth brushed gently with a nylon paint brush with bristles cut to a 1" length. The side of the sieve frame may be tapped gently with the handle of the brush to dislodge the particles between brush strokes. At no time should a needle or other sharp object be used to remove the particles lodged in the wire cloth. Special care should be taken when brushing sieves finer than 80 mesh. Brushing can cause distortions and irregularities in the mesh. The procedure is repeated for each sieve in the stack and contents of the pan.

The individual weights retained on the sieves should be added and compared to the starting sample weight. Wide variations or sample losses should be determined immediately. Compare the weights on each sieve with the total sample weight and calculate the percentage of the total retained at that point.

Presentation and analysis of the resulting data is frequently made easier by plotting on one of a number of graph formats. The most common graphic presentation is the plot of the cumulative percentage of material retained on a screen (plotted on a logarithmic scale) versus percentage (plotted on a linear scale). The resulting curve allows a quick approximation of the sieve size at the fifty percentile point of accumulation. The curve also shows the smoothness of the distribution by revealing the presence of bimodal blends in the sample. Other plotting techniques include log-log and direct plotting of micron size versus percentage retained.



COMMONLY USED BRUSHING TECHNIQUE

Care should be exercised in the analysis of the data in relation to the length of time the test was run. If your sample contains a large amount of elongated or near-size particles, the test results can be misleading. The longer the sieving interval, the greater the percentage of these problem particles passing through the screens. Ideally each fraction should be inspected microscopically after sieving to determine the integrity of the sieve cut point.

Table 6 lists the ASTM published standards on sieve analysis procedures for specific materials or industries.

CHAPTER 7

SIEVE CARE AND CLEANING

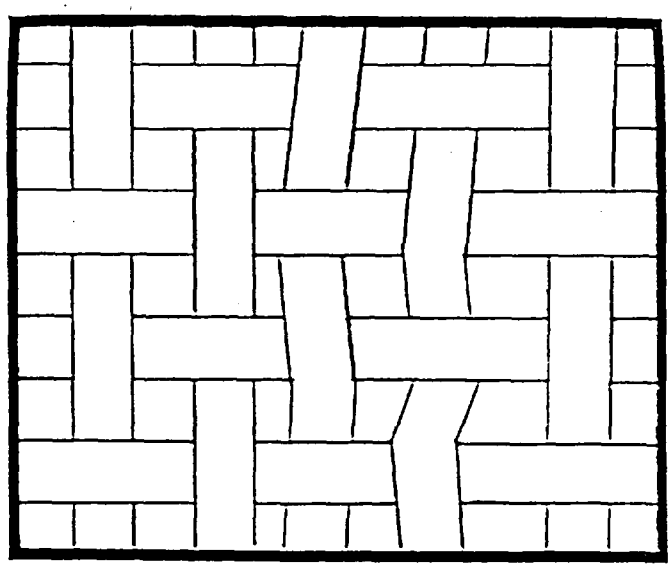
Test sieves, like any other piece of analytical laboratory equipment, require regular care to maintain their performance standards. The sieves should be kept clean and dry at all times, and stored either in the cardboard carton provided or in a suitable cabinet. In order for the test sieve to perform properly, the wire cloth must be taut and free from variations in opening size. For this reason, cleaning procedures must be clearly delineated as part of a comprehensive sieving program.

Test sieves should be cleaned ultrasonically on a regular basis. For some installations, this may be done at the end of a shift or at the end of a week, but must be done regularly to assure good sieving results. The sieves should be immersed in an ultrasonic cleaner filled with a solution of a mild detergent and water. The sieves should be cleaned for a suitable time interval (follow manufacturer's instructions). Before using, allow the test sieves to dry thoroughly. Regular ultrasonic cleaning will prevent the buildup of particles trapped in the mesh and prolong the useful life of the sieve. For between test clean-up, brushing of the mesh, sizes 100 and coarser, is allowable. For best results, use a nylon bristle paint brush with the bristles cut to a length of approximately 1". The mesh should be brushed from the underside only with a gentle circular motion. Vigorous brushing will distort the sieve openings and reduce the effective life of the sieve. Under no circumstances should particles lodged in the sieve openings be removed with a sharp object. These particles should be removed in an ultrasonic cleaner only. Brushing should be avoided on sieves finer than 100 mesh, as the fine wires are more likely to bend, distort or even break. Brushing has a tendency to loosen any wire cloth, but the fine ranges are even more susceptible to this damage.

Similarly, cleaning sieves with a compressed air jet is common, but can be disastrous to the 100 mesh and finer range. The concentrated jet of air can do severe 'local' damage to the wire cloth, and significantly loosen the wire cloth.

Generally, sieves can have an effective life of many years with proper care. The wear that occurs over time does not change the opening sizes, but does abrade the 'knuckles' or crimps of the mesh. A sieve with a noticeable sag to the mesh should be replaced. Fine mesh sieves that have torn should not be resoldered, as the localized heat of the soldering iron can distort the openings. Epoxies have been used for repairs, but usually tend to block a large percentage of the openings. The typical epoxies also become too brittle for the flexing of the wire cloth and can fracture with use.

Good general laboratory procedure should be observed with testing sieves as with any other piece of test equipment. Testing should be performed with clean, uncontaminated sieves, especially when using a sieve for the first time. With proper care and cleaning coupled with a good calibration procedure, any test sieve should provide many years of consistent service.



WIRE CLOTH DAMAGED BY IMPROPER BRUSHING

Note the irregularities in both opening size and shape.

EPILOG

We hope that the characterization of testing sieves and their uses presented in this manual will serve as an enhancement to your current particle size analysis program. By maximizing the analytical advantage potential of testing sieves while minimizing and compensating for shortcomings and inaccuracies, the testing sieve can be a viable and precise testing tool. Care, maintenance and proper test procedure are as critical with a testing sieve as they are with other, more sophisticated particle size analyzers.

Compliance with applicable industry, National and International specifications is essential. The intent of these regulating bodies is the formulation of general standards to assure uniformity in testing standards observed by both buyer and producer. The accepted specification should be the foundation for the in-house testing procedure.

Testing accuracy is highly dependent on the technique of the operators. Interpretation of data should be neither overstated nor understated in terms of importance. The effects of variables must be understood, accepted and factored into final data analysis to avoid these shortcomings.

By analyzing the total test sieve analysis program as we suggest from sample preparation to data presentation, variations can be reduced, accuracy improved, and productivity increased.

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U. S. A. STANDARD SIEVES ASTM SPECIFICATION E-11

Nominal Dimensions, Permissible Variations for Wire Cloth of Standard Test Sieves (U.S.A.) Standard Series

Sieve Designation (W)		Nominal Sieve Opening, in.[c]	Permissible Variation of Average Opening from the Standard Sieve Designation (y)	Intermediate Tolerance (z)[g]	Maximum Individual Opening (x)	Nominal Wire Diameter, mm[g]
Standard[b]	Alternative					
(1)	(2)	(3)	(4)	(5)	(6)	(7)
125 mm	5 in.	5	±3.7 mm	130.0 mm	130.9 mm	8.00
106 mm	4.24 in.	4.24	±3.2 mm	110.2 mm	111.1 mm	6.40
100 mm[d]	4 in.[d]	4	±3.0 mm	104.0 mm	104.8 mm	6.30
90 mm	3½ in.	3.5	±2.7 mm	93.6 mm	94.4 mm	6.08
75 mm	3 in.	3	±2.2 mm	78.1 mm	78.7 mm	5.50
63 mm	2½ in.	2.5	±1.9 mm	65.6 mm	66.2 mm	5.50
53 mm	2.12 in.	2.12	±1.6 mm	55.2 mm	55.7 mm	5.15
50 mm[d]	2 in.[d]	2	±1.5 mm	52.1 mm	52.6 mm	5.05
45 mm	1¾ in.	1.75	±1.4 mm	46.9 mm	47.4 mm	4.85
37.5 mm	1½ in.	1.5	±1.1 mm	39.1 mm	39.5 mm	4.59
31.5 mm	1¼ in.	1.25	±1.0 mm	32.9 mm	33.2 mm	4.23
26.5 mm	1.06 in.	1.06	±0.8 mm	27.7 mm	28.0 mm	3.90
25.0 mm[d]	1 in.[d]	1	±0.8 mm	26.1 mm	26.4 mm	3.80
22.4 mm	⅞ in.	0.875	±0.7 mm	23.4 mm	23.7 mm	3.50
19.0 mm	¾ in.	0.750	±0.6 mm	19.9 mm	20.1 mm	3.30
16.0 mm	⅝ in.	0.625	±0.5 mm	16.7 mm	17.0 mm	3.00
13.2 mm	0.530 in.	0.530	±0.41 mm	13.83 mm	14.05 mm	2.75
12.5 mm[d]	½ in.[d]	0.500	±0.39 mm	13.10 mm	13.31 mm	2.67
11.2 mm	7/16 in.	0.438	±0.35 mm	11.75 mm	11.94 mm	2.45
9.5 mm	⅜ in.	0.375	±0.30 mm	9.97 mm	10.16 mm	2.27
8.0 mm	5/16 in.	0.312	±0.25 mm	8.41 mm	8.58 mm	2.07
6.7 mm	0.265 in.	0.265	±0.21 mm	7.05 mm	7.20 mm	1.87
6.3 mm[d]	¼ in.[d]	0.250	±0.20 mm	6.64 mm	6.78 mm	1.82
5.6 mm	No. 3½[e]	0.223	±0.18 mm	5.90 mm	6.04 mm	1.68
4.75 mm	No. 4	0.187	±0.15 mm	5.02 mm	5.14 mm	1.54
4.00 mm	No. 5	0.157	±0.13 mm	4.23 mm	4.35 mm	1.37
3.35 mm	No. 6	0.132	±0.11 mm	3.55 mm	3.66 mm	1.23
2.80 mm	No. 7	0.11	±0.095 mm	2.975 mm	3.070 mm	1.10
2.36 mm	No. 8	0.0937	±0.080 mm	2.515 mm	2.600 mm	1.00
2.00 mm	No. 10	0.0787	±0.070 mm	2.135 mm	2.215 mm	0.900
1.70 mm	No. 12	0.0661	±0.060 mm	1.820 mm	1.890 mm	0.810
1.40 mm	No. 14	0.0555	±0.050 mm	1.505 mm	1.565 mm	0.725
1.18 mm	No. 16	0.0469	±0.045 mm	1.270 mm	1.330 mm	0.650
1.00 mm	No. 18	0.0394	±0.040 mm	1.080 mm	1.135 mm	0.580
850 μm[f]	No. 20	0.0331	±35 μm	925 μm	970 μm	0.510
710 μm	No. 25	0.0278	±30 μm	775 μm	815 μm	0.450
600 μm	No. 30	0.0234	±25 μm	660 μm	695 μm	0.390
500 μm	No. 35	0.0197	±20 μm	550 μm	585 μm	0.340
425 μm	No. 40	0.0165	±19 μm	471 μm	502 μm	0.290
355 μm	No. 45	0.0139	±16 μm	396 μm	425 μm	0.247
300 μm	No. 50	0.0117	±14 μm	337 μm	363 μm	0.215
250 μm	No. 60	0.0098	±12 μm	283 μm	306 μm	0.180
212 μm	No. 70	0.0083	±10 μm	242 μm	263 μm	0.152
180 μm	No. 80	0.0070	±9 μm	207 μm	227 μm	0.131
150 μm	No. 100	0.0059	±8 μm	174 μm	192 μm	0.110
125 μm	No. 120	0.0049	±7 μm	147 μm	163 μm	0.091
106 μm	No. 140	0.0041	±6 μm	126 μm	141 μm	0.076
90 μm	No. 170	0.0035	±5 μm	108 μm	122 μm	0.064
75 μm	No. 200	0.0029	±5 μm	91 μm	103 μm	0.053
63 μm	No. 230	0.0025	±4 μm	77 μm	89 μm	0.044
53 μm	No. 270	0.0021	±4 μm	66 μm	76 μm	0.037
45 μm	No. 325	0.0017	±3 μm	57 μm	66 μm	0.030
38 μm	No. 400	0.0015	±3 μm	48 μm	57 μm	0.025
32 μm	No. 450	0.0012	±3 μm	42 μm	50 μm	0.028
25 μm	No. 500	0.0010	±3 μm	34 μm	41 μm	0.025
20 μm	No. 635	0.0008	±3 μm	29 μm	35 μm	0.020

[a] The average diameter of the warp and of the shoot wires, taken separately, of the cloth of any sieve shall not deviate from the nominal values by more than the following:

Sieves coarser than 600 μm	5 percent
Sieves 600 to 125 μm	7½ percent
Sieves finer than 125 μm	10 percent

[b] These standard designations correspond to the values for test sieve apertures recommended by the International Standards Organization, Geneva, Switzerland.

[c] Only approximately equivalent to the metric values in Column 1.

[d] These sieves are not in the standard series but they have been included because they are in common usage.

[e] These numbers (3½ to 635) are the approximate number of openings per linear inch but it is preferred that the sieve be identified by the standard designation in millimeters or micrometers.

[f] 1000 μm — 1 mm.

[g] Not more than 5% of the openings may fall between the limits set by the values in Column 5 and Column 6.

Table 1

INTERNATIONAL STANDARDS ORGANIZATION
PREFERRED NUMBER SERIES

R 10	Basic sizes millimeters R 20	R 40	Equivalent sizes (for information) inches
1.00	1.00	*1.00	0.039 4
		1.06	0.041 7
	1.12	1.12	0.044 1
		*1.18	0.046 5
1.25	1.25	1.25	0.049 2
		1.32	0.052 0
	1.40	*1.40	0.055 2
		1.50	0.059 1
1.60	1.60	1.60	0.063 0
		*1.70	0.066 9
	1.80	1.80	0.070 9
		1.90	0.074 8
2.00	2.00	*2.00	0.078 7
		2.12	0.083 5
	2.24	2.24	0.088 2
		*2.36	0.092 9
2.50	2.50	2.50	0.098 4
		2.65	0.104 3
	2.80	*2.80	0.110 2
		3.00	0.118 1
3.15	3.15	3.15	0.124 0
		*3.35	0.131 9
	3.55	3.55	0.139 8
		3.75	0.147 6
4.00	4.00	*4.00	0.157 5
		4.25	0.167 3
	4.50	4.50	0.177 2
		4.75	0.187 0
5.00	5.00	5.00	0.196 9
		5.30	0.208 7
	5.60	*5.60	0.220 5
		6.00	0.236 2
6.30	6.30	6.30	0.248 0
		*6.70	0.263 8
	7.10	7.10	0.279 5
8.00	8.00	*8.00	0.315 0
		8.50	0.334 6
	9.00	9.00	0.354 3
		*9.50	0.374 0
10.00	10.00	10.00	0.393 7
		10.6	0.417 3
	11.2	*11.2	0.440 9
			0.464 6
		11.8	
12.5	12.5	12.5	0.492 1
		*13.2	0.519 7
	14.0	14.0	0.551 8
		15.0	0.590 6
16.0	16.0	*16.0	0.629 9
		17.0	0.669 3
	18.0	18.0	0.708 7
		*19.0	0.748 0
20.0	20.0	20.0	0.787 4
		21.2	0.834 6
	22.4	*22.4	0.881 9
		23.6	0.929 1
25.0	25.0	25.0	0.984 3

Table 2

* — R-40/3 Series - Every third number of R-40 Series. Same as ASTM E-11 USA Standard Sieve Series.

R-10 — Tenth Root of ten ratio

R-20 — Twentieth root of ten

R-40 — Fortieth root of ten

COMPARISON TABLE
INTERNATIONAL TEST SIEVE SERIES

INTERNATIONAL ISO 565 (TBL2): 1983	AMERICAN ANSI/ASTM E-11-81		BRITISH BS 410: 1976		CANADA 8-GP-2M: 1976	FRENCH AFNOR NEX 11-501: 1970	GERMAN DIN 4188: 1977
Aperture mm	Opening mm	Equivalent inch/Number	Aperture mm	Equivalent BS Mesh	Aperture mm	Aperture mm	Aperture mm
	106.00	4.24"	106.00				
100.00	100.00	4.0"	100.00		100.00	100.00	100.00
90.00	90.00	3 1/2"	90.00		90.00	90.00	90.00
71.00	75.00	3"	75.00		71.00	71.00	71.00
63.00	63.00	2 1/2"	63.00		63.00	63.00	63.00
	53.00	2.12"	53.00		53.00	53.00	53.00
50.00	50.00	2.0"	50.00		50.00	50.00	50.00
45.00	45.00	1 3/4"	45.00		45.00	45.00	45.00
	37.50	1 1/2"	37.50				
31.50	31.50	1 1/4"	31.50		31.50	31.50	31.50
26.50	26.50	1.06"	26.50		28.00*	28.00*	28.00*
–	25.00	1.00"	25.00		25.00	25.00	25.00
22.40	22.40	7/8"	22.40		22.40	22.40	22.40
19.00	19.00	3/4"	19.00		20.00*	20.00*	20.00*
16.00	16.00	5/8"	16.00		16.00	16.00	16.00
13.20	13.20	.530"	13.20		14.00*	14.00*	14.00*
–	12.50	1/2"	12.50		12.50	12.50	12.50
11.20	11.20	7/16"	11.20		11.20	11.20	11.20
9.50	9.50	3/8"	9.50		10.00*	10.00*	10.00*
8.00	8.00	5/16"	8.00		8.00	8.00	8.00
6.70	6.70	.265"	6.70		7.10*	7.10*	7.10*
–	6.30	1/4"	6.30		6.30	6.30	6.30
5.60	5.60	No. 3 1/2	5.60	3	5.60	5.60	5.60
4.75	4.75	4	4.75	3 1/2	–	–	–
4.00	4.00	5	4.00	4	4.00	4.00	4.00
3.35	3.35	6	3.35	5	3.15*	3.15*	3.15*
2.80	2.80	7	2.80	6	2.80	2.80	2.80
2.36	2.36	8	2.36	7	2.50*	2.50*	2.50*
2.00	2.00	10	2.00	8	2.00	2.00	2.00
1.70	1.70	12	1.70	10	1.60*	1.60*	1.60*
1.40	1.40	14	1.40	12	1.40	1.40	1.40
1.18	1.18	16	1.18	14	1.12*	1.12*	1.12*
1.00	1.00	18	1.00	16	1.00	1.00	1.00
850µm	850µm	20	850µm	18	800*µm	800*µm	800*µm
710µm	710µm	25	710µm	22	710µm	710µm	710µm
600µm	600µm	30	600µm	25	–	–	–
500µm	500µm	35	500µm	30	500µm	500µm	500µm
425µm	425µm	40	425µm	36	400*µm	400*µm	400*µm
355µm	355µm	45	355µm	44	355µm	355µm	355µm
300µm	300µm	50	300µm	52	315*µm	315*µm	315*µm
250µm	250µm	60	250µm	60	250µm	250µm	250µm
212µm	212µm	70	212µm	72	200*µm	200*µm	200*µm
180µm	180µm	80	180µm	85	180µm	180µm	180µm
150µm	150µm	100	150µm	100	140*µm	140*µm	140*µm
125µm	125µm	120	125µm	120	125µm	125µm	125µm
106µm	106µm	140	106µm	150	100*µm	100*µm	100*µm
90µm	90µm	170	90µm	170	90µm	90µm	90µm
75µm	75µm	200	75µm	200	71*µm	71*µm	71*µm
63µm	63µm	230	63µm	240	63µm	63µm	63µm
53µm	53µm	270	53µm	300	56*µm	56*µm	56*µm
45µm	45µm	325	45µm	350	45µm	45µm	45µm
38µm	38µm	400	38µm	400	36*µm	36*µm	36*µm

Closest equivalent to ISO 565 (TBL 2)

Table 3

RECOMMENDED REPRESENTATIVE BULK VOLUMES OF TEST SAMPLES

Used In 8" (203mm) Testing Sieves

Standard Sieve Designation		Bulk Volume of Material	
Standard	Alternate	*Recommended Volume of Material for Test Sample*	*Maximum Permitted Volume on Sieve on Completion of Sieving*
1	2	3	4
25.0mm	1 in.	1800cm³	900cm³
22.4	7/8	1600	800
19.0	3/4	1400	700
16.0	5/8	1000	500
12.5	1/2	800	400
11.2	7/16	800	400
9.5	3/8	600	300
8.0	5/16	500	250
6.30	1/4	400	200
5.60	No. 3 1/2	400	200
4.0	No. 5	350	150
2.80	No. 7	240	120
2.0	No. 10	200	100
)	No. 14	160	80
1.0	No. 18	140	70
710μm	No. 25	120	60
500	No. 35	100	50
355	No. 45	80	40
250	No. 60	70	35
180	No. 80	60	30
125	No. 120	50	25
90	No. 170	40	20
63	No. 230	35	17
45	No. 325	30	15
38	No. 400	25	12

The recommended weight of material for a sieve test sample is calculated by multiplying the bulk volume figure in Column 3 by the particular bulk density in grams per cubic centimeter of the material, rounded out within a tolerance of ±25 percent.

Table 4

BULK DENSITY OF PULVERIZED MATERIALS IN FREELY POURED CONDITION[a]

Material	Avg. Wt. lbs/ft³	Avg. Wt. g/cm³	Material	Avg. Wt. lbs/ft³	Avg. Wt. g/cm³	Material	Avg. Wt. lbs/ft³	Avg. Wt. g/cm³
Alumina	44	1.23	Garnet	168	2.69	Salt, rock	66	1.06
Aluminum,			Glass beads	76	1.22	Salt, table	75	1.20
calcined	128	2.05	Glass, crushed	66	1.06	Sand	90 to 100	1.44 to 1.60
Aluminum oxide	122	1.96	Glass cullet	93	1.49	Sand, silica	90 to 100	1.44 to 1.60
Aluminum shot	96	1.54	Granite,			Sawdust	13	0.21
Ammonium nitrate	48	0.77	crushed	95 to 100	1.52 to 1.60	Seacoal	42	0.67
Ammonium - sulfate			Gravel	90 to 100	1.44 to 1.60	Shale	100	1.60
	61	0.98	Gypsum, calcined	58	0.93	Shot, metal	220	3.69
Asbestos ore	54	0.87	Gypsum,			Silica flour	27	0.43
Bauxite ore	75 to 85	1.20 to 1.36	crushed	90 to 100	1.44 to 1.60	Silica gel	45	0.72
Bentonite	50 to 65	0.80 to 1.04	Iron ore	120 to 150	1.92 to 2.40	Soapstone,		
Bicarbonate of soda	57	0.91	Kaolin	160	2.56	pulverized	40	0.64
Borax	50 to 61	0.80 to 0.98	Kyanite	68	1.09	Soda ash,		
Boric acid	58	0.93	Lime, ground	60 to 60	0.96	light	25 to 35	0.40 to 0.56
Calcite	90 to 105	1.44 to 1.68	Lime, hydrated	25	0.40	Soda ash, heavy	55 to 65	0.88 to 1.04
Calcium carbide	75	1.20	Limestone, crushed	85 to 100	1.36 to 1.60	Soda, bicarbonate	57	0.91
Calcium carbonate	49	0.79	Limestone, agricultural	70	1.12	Sodium nitrate	78	1.25
Calcium chloride	64	1.03	Magnesite	106	1.70	Sodium phosphate	43	0.69
Calcium phosphate	57	0.91	Magnetite	155	2.49	Sodium sulfate	96	1.54
Carbon black	24	0.33	Manganese ore	120 to 136	1.92 to 2.18	Steel grit	228	3.66
Cellulose powder	16	0.26	Marble, crushed	90 to 95	1.44 to 1.52	Stone, crushed	85 to 95	1.36 to 1.52
Cement,			Metals, powdered			Sugar, granulated	50	0.80
portland	90 to 100	1.44 to 1.60	Aluminum	80	1.28	Sugar, powdered	37	0.59
Cement clinker	75 to 80	1.20 to 1.28	Copper	169	2.71	Sulphur, crushed	50 to 65	0.80 to 1.04
Chrome ore	140	2.25	Copper-lead	364	5.84	Talc, powder	34	0.55
Clay	30 to 75	0.48 to 1.20	Iron	243	3.90	Talc, granular	44	0.71
Coal, anthracite	55	0.88	Nickel	263	4.22	Traprock, crushed	105 to 110	1.68 to 1.76
Coal, bituminous	50	0.88	Stainless steel	240	3.85			
Coke breeze	25 to 35	0.40	Tantalum	300	4.80	Triple superphos-		
Coke,			Mica	42	0.67	phate, granular	64	1.03
petroleum	25 to 40	0.40 to 0.64	Ore, sintered	144	1.83	Tungsten carbide	550	8.82
Copper ore	100 to 150	1.60 to 2.40	Oyster shells, ground	29	0.47	Urea prills	43	0.69
Coquina shell	80	1.28	Perlite ore	65 to 75	1.04 to 1.20	Vermiculite ore	80	1.28
Corn starch	40	0.64	Plaster, calcined	64	1.03	Wood chips	13	0.21
Diatomaceous earth	31	0.50	Polyethylene pellets	36	0.58	Zinc dust	144	2.31
Dicalcium phosphate	64	1.03	Polyethylene powder	18	0.29	Zirconium oxide	200	3.22
Dolomite,			Poly (vinyl			Zirconium sand	162	2.60
crushed	90 to 100	1.44 to 1.60	chloride)	30	0.48			
Feldspar, crushed	63 to 84	1.04 to 1.35	Potash	77	1.23			
Ferrophosphorous	196	3.14	Potassium					
Fire clay	80	1.28	carbonate	79	1.27			
Flour, wheat	24	0.38	Pumice	40	0.64			
Flour, maize	37	0.59	Rubber, chopped	36	0.58			
Fluorspar	90 to 120	1.44 to 1.92	Rubber, ground	20	0.32			
Fly ash	49	0.79	Phosphate rock	75 to 85	1.20 to 1.36			
Fullers earth	30 to 40	0.48 to 0.64	Salt, flake	61	0.98			

a — Where a single figure is given, it represents an actual weight of a typical average sample of the material recorded by a research laboratory; therefore, the figure can be expected to vary from sample to sample of the same material.

Table 5

LIST OF ASTM PUBLISHED STANDARDS ON SIEVE ANALYSIS PROCEDURES FOR SPECIFIC MATERIALS OR INDUSTRIES

Material	ASTM Designation	Title of Standard	Sieve No. or Size Range	Dry	Wet
Aggregates	C 117	Test for Materials Finer Than No. 200 Sieve in Mineral Aggregates by Washing [a]	200		X
	C 125	*Definitions of Terms Relating to* Concrete and Concrete Aggregates			
	C 136	Test for Sieve or Screen Analysis of Fine and Coarse Aggregates [a]	3½ in.-200	X	
	C 142	Test for Friable Particles in Aggregates	1½ in.-20	X	
	C 330	Specifications for Lightweight Aggregates for Structural Concrete	1 in.-100	X	X
	C 331	Specifications for Lightweight Aggregates for Concrete Masonry Units	3/4 in.-100	X	X
Asbestos	D 2589	Test for Bauer-McNett Wet Classification of Asbestos Fiber	4-325		X
Asphalt	D 313	Test for Coarse Particles in Mixtures of Asphalt and Mineral Matter			X
Carbon black	D 1508	Test for Fines Content of Pelleted Carbon Black	100	X	
	D 1511	Test for Pellet Size Distribution of Carbon Black	10-120	X	
	D 1514	Test for Sieve Residue from Carbon Black	30-325		X
Casein	D 2592	Test for Sieve Analysis of Dasein and Isolated Soy Protein	4-200	X	
Ceramic [b]	C 325	Method for Wet Sieve Analysis of Ceramic Whiteware Clays	100-325		X
	C 371	Method for Sieve Analysis of Nonplastic Pulverized Ceramic Materials [a]	70-325		X
Coal	D 197	Sampling and Fineness Test of Powdered Coal [a]	16-200	X	
	D 310	Test for Size of Anthracite [a]	4 3/8 in.-3/16 in.	X	
	D 311	Test for Sieve Analysis of Crushed Bituminous Coal [a]	1 in.-6	X	
	D 410	Test for Screen Analysis of Coal [a]	8 in.-200	X	
	D 431	Method of Designating the Size of Coal from its Analysis	8 in.-200	X	
Coke	D 293	Test for Sieve Analysis of Coke [a]	4 in.-0	X	
Cement	C 184	Test for Fineness of Hydraulic Cement by the No. 100 and 200 Sieves	100 200	X	
	C 430	Test for Fineness of Hydraulic Cement by the No. 325 Sieve	325		X
Enamel	C 285	Method for Sieve Analysis of Wet Milled and Dry Milled Porcelain Enamel	40-325	X	X
Glass	C 429	Method for Sieve Analysis of Raw Materials for Glass Manufacture [a]	8-200	X	X
	D 1214	Test for Sieve Analysis of Glass Spheres			
Magnesia	C 239	Test for Sieve Analysis of Plastic Calcined Magnesia	200		X
Magnesium compositions	C 238	Method for Sieve Analysis of Magnesium Oxychloride Compositions, Aggregates and Fillers		X	
Metal Bearing ores	E 276	Test for Particle Size or Screen Analysis at No. 4 Sieve and Finer for Metal Bearing Ores and Related Materials [a]	4-200	X	X
Metal powders	B 214	Test for Sieve Analysis of Granular Metal Powders	60-325	X	
Mineral	D 451	Test for Sieve Analysis of Granular Mineral Surfacing for Asphalt Roofing and Shingles [a]	6-100	X	
	D 452	Test for Sieve Analysis of Nongranular Mineral Surfacing for Asphalt Roofing and Shingles [a]	12-200	X	
	D 546	Test for Sieve Analysis of Mineral Filler		X	
Perlite	C 549	Specification for Perlite Loose Fill Insulation [a]		X	
Pigments and paint	D 185	Tests for Coarse Particles in Pigments, Pastes and Paints	325	X	X
	D 480	Methods of Sampling and Testing Aluminum Powder and Paste [a]	100-325		X
Plastic	D 1921	Test for Particle Size (Sieve Analysis) of Plastic Materials		X	
Refractories	C 92	Tests for Sieve Analysis and Water Content of Refractory Materials	3-200	X	X
Resins	D 1457	Specification for TFE-Fluorocarbon Resin Molding and Extrusion Materials	18-325		X
	D 1705	Method for Particle Size Analysis of Powdered Polymers and Copolymers of Vinyl Chloride			X
	D 2187	Tests for Physical and Chemical Properties of Ion-Exchange Resins [a]	8-100		X
Soap	D 502	*Test for Particle Size of* Soaps and Other Detergents	12-100	X	
Soil	D 421	Method for Dry Preparation of Soil Samples for Grain-Size Analysis and Determination of Soil Constants	4-40		X
	D 422	Method for Grain-Size Analysis of Soils	3 in.-200		X
	D 1140	Test for Amount of Material in Soils Finer Than the No. 200 Sieve	40-200		X
	D 2217	Method for Wet Preparation of Soil Samples for Grain-Size Analysis and Determination of Soil Constants	10-40		X
Vermiculite	C 516	Specifications for Vermiculite Loose Fill Insulation [a]	3/4-100	X	

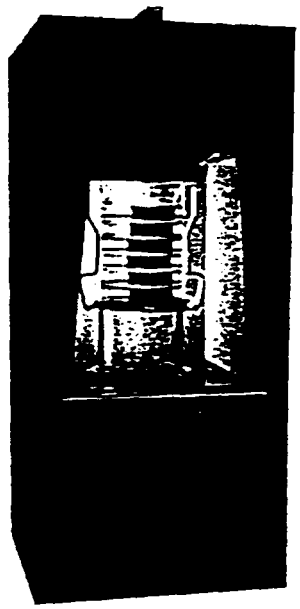
a — Contains suggestions on sampling.

b — Also, C 623, Method for Precision Electroformed Wet Sieve Analysis of Nonplastic Ceramic Powders.

Table 6

Other products available from the publisher of this manual:

THE ATM SONIC SIFTERS



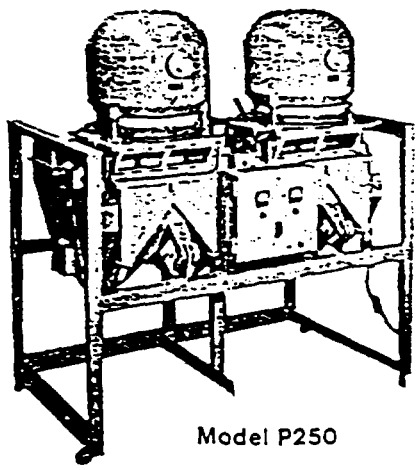
The Model L3P Laboratory Sonic Sifter

A viable alternative for fine powder sieving using a unique oscillating air column. The effective size range is 5660 μm (3.5 mesh) through 5 μm using 3" diameter acrylic frame sieve. This method has the advantages of high accuracy with low test times, while showing no signs of particle attrition or screen wear.

Model P60

The Model P60 Production Sonic Sifter

60 square inches of screening area are available in this single screen, single pass continuous feed sonic sifter. The effective screening range is 5660 μm (3.5 mesh) through 20 μm (635 mesh). Ideal for pilot plant and small production application, this modular sifter is capable of input rates of up to several hundred pounds per hour.

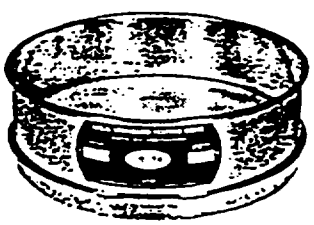


Model P250

The Model P250 Production Sonic Sifter

Two 125 square inch screening modules provide input rates of up to 1000 pounds per hour in this high accuracy, single pass sifter. An upscaled version of the model P60.

This manual was edited by Scott Nushart and Walter Mahlig.



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WARZYN

SIEVE ANALYSIS ASTM C136-84
COMPUTER CALCULATION SHEET

JOB:

Job No. _____
Date _____
Sheet _____ of _____
Techs _____
Checked By _____

BORING/SAMPLE									
PAN NO.									
START WT. or HYD (No Tare)									
END WT./REMARKS (No Tare)									
1 1/2									
1									
3/4									
1/2									
3/8									
#4									
#8									
#10									
#16									
#30									
#40									
#50									
#80									
#100									
#200									

note: all technicians performing work are required to initial sheet.

WARZYN

SIEVE ANALYSIS

JOB:

SAMPLE NO.

PAN NO.

Report No. _____

Job No. _____

Date _____

Sheet _____ of _____

Start Sample Weight =

End Sample Weight = _____

Weight of P200 Loss =

$\frac{\text{P200 Loss Weight}}{\text{Start Sample Weight}}$ = % P200 Loss

End Sample Weight =

R #4 Sieve Weight = _____

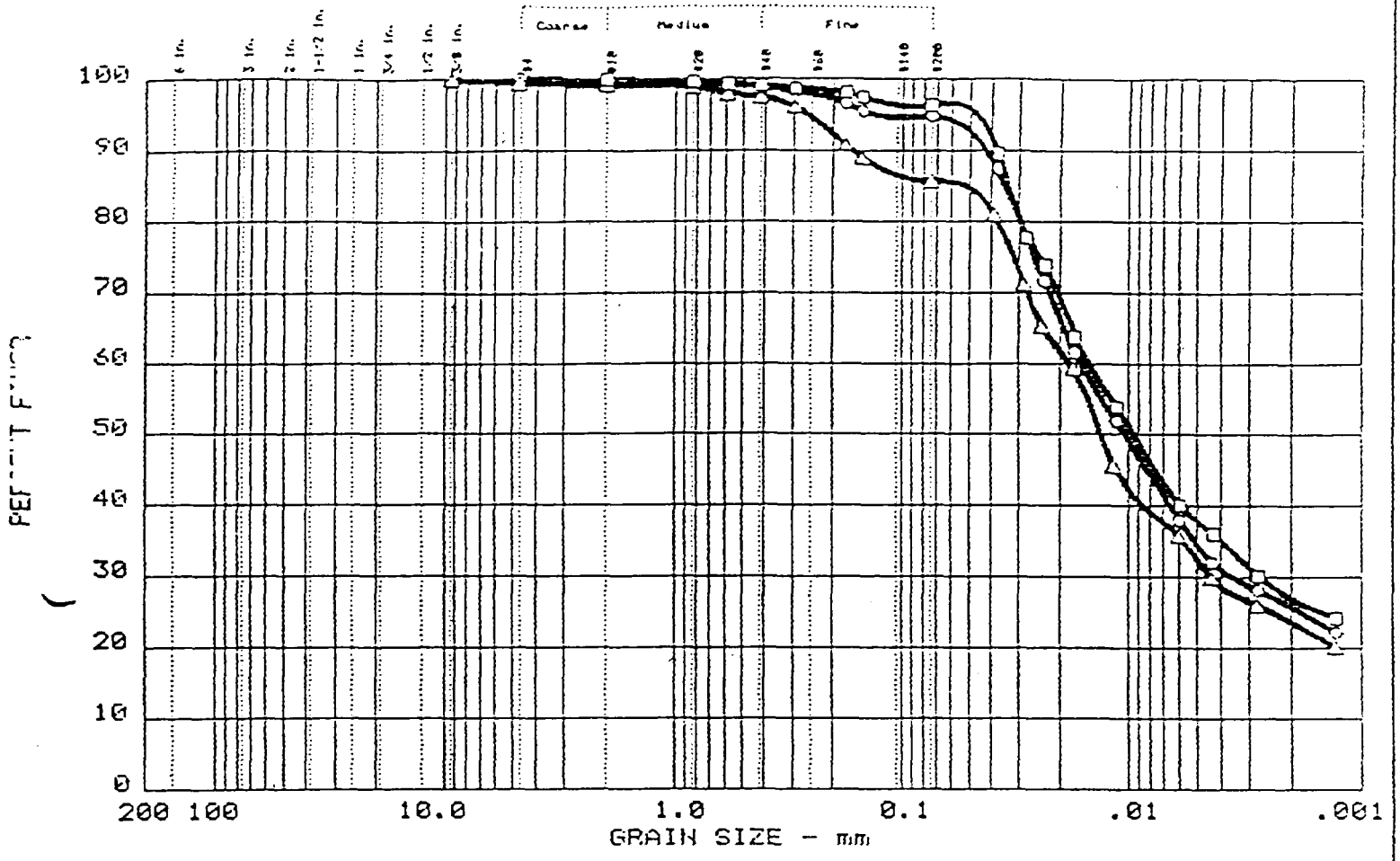
Difference in Weight =

$\frac{\text{Weight Difference}}{\text{Start Sample Weight}}$ = Mult

Sieve Size	Comm. Wt. Retained	Percent Passing	Multiplier	% P200 Loss in Washing	Percent Passing	_____ Specifications
2 1/2"		X	X	X		
2"		X	X	X		
1 1/2"		X	X	X		
1"		X	X	X		
3/4"		X	X	X		
1/2"		X	X	X		
3/8"		X	X	X		
#4		X	X	X		
Quartered P#4 Wt =						
#4						
#8						
#10						
#16						
#30						
#40						
#50						
#80						
#100						
#200						

DA/mlf
[WEI-15-35]

GRAIN SIZE DISTRIBUTION TEST REPORT



Symbol	%+3"	% GRAVEL	% SAND	% SILT	% CLAY
○	0.0	0.0	5.2	60.4	34.4
△	0.0	0.6	13.8	53.3	32.4
□	0.0	0.0	3.7	58.5	37.8

	LL	PI	D_{85}	D_{60}	D_{50}	D_{30}	D_{15}	D_{10}	C_c	C_u
○	39	19			0.01	0.004				
△	36	16			0.01	0.004				
□	44	21			0.01	0.003				

MATERIAL DESCRIPTION	USCS
○ Brown Lean CLAY, Little Sand	CL
△ Brown Lean CLAY, Some Sand, Trace Gravel	CL
□ Brown Lean CLAY, Trace Sand	CL

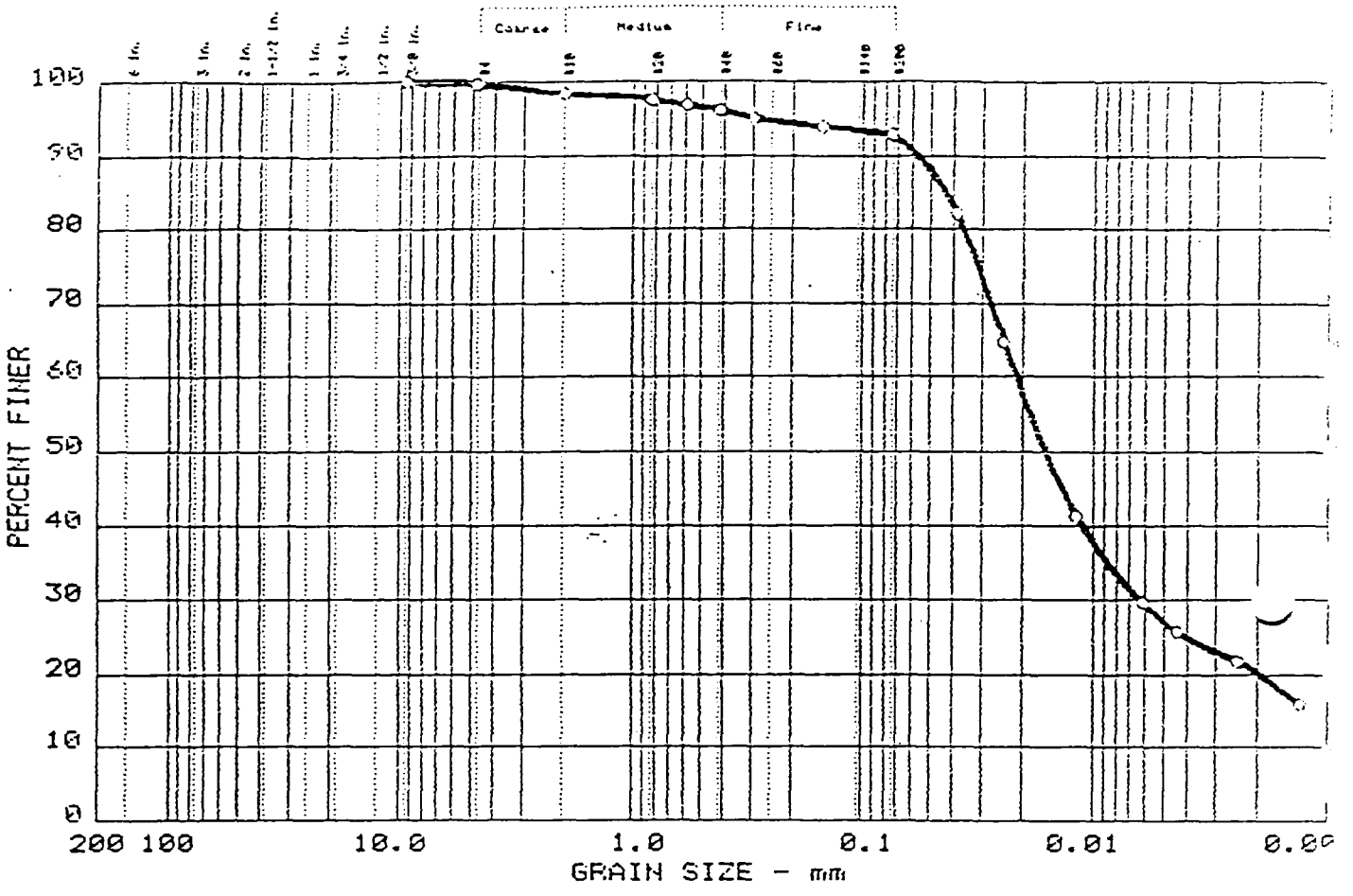
Project No.: 5822.41
Project:
○ Sample: TP-1 SAMPLE # 3 @ 1.5-3.0 FT
△ Sample: TP-2 SAMPLE # 3 @ 1.0-2.5 FT
□ Sample: TP-3 SAMPLE # 3 @ 1.0-2.5 FT
Date: 5/14/91

GRAIN SIZE DISTRIBUTION TEST REPORT
WARZYN ENGINEERING INC.

Remarks:
TESTED BY DWA/RP
CHECKED BY DWA
APPROVED BY VJR

Sheet No.

GRAIN SIZE DISTRIBUTION TEST REPORT



Symbol	% +3"	% GRAVEL	% SAND	% SILT	% CLAY
○	0.0	0.3	6.7	66.0	27.0

	LL	PI	D_{85}	D_{60}	D_{50}	D_{30}	D_{15}	D_{10}	C_c	C_u
○	37	15			0.02	0.006				

MATERIAL DESCRIPTION	USCS
○ Brown Lean CLAY, Little Sand	CL

Project No.: 12153.01
Project:
○ Sample: Sample # 11

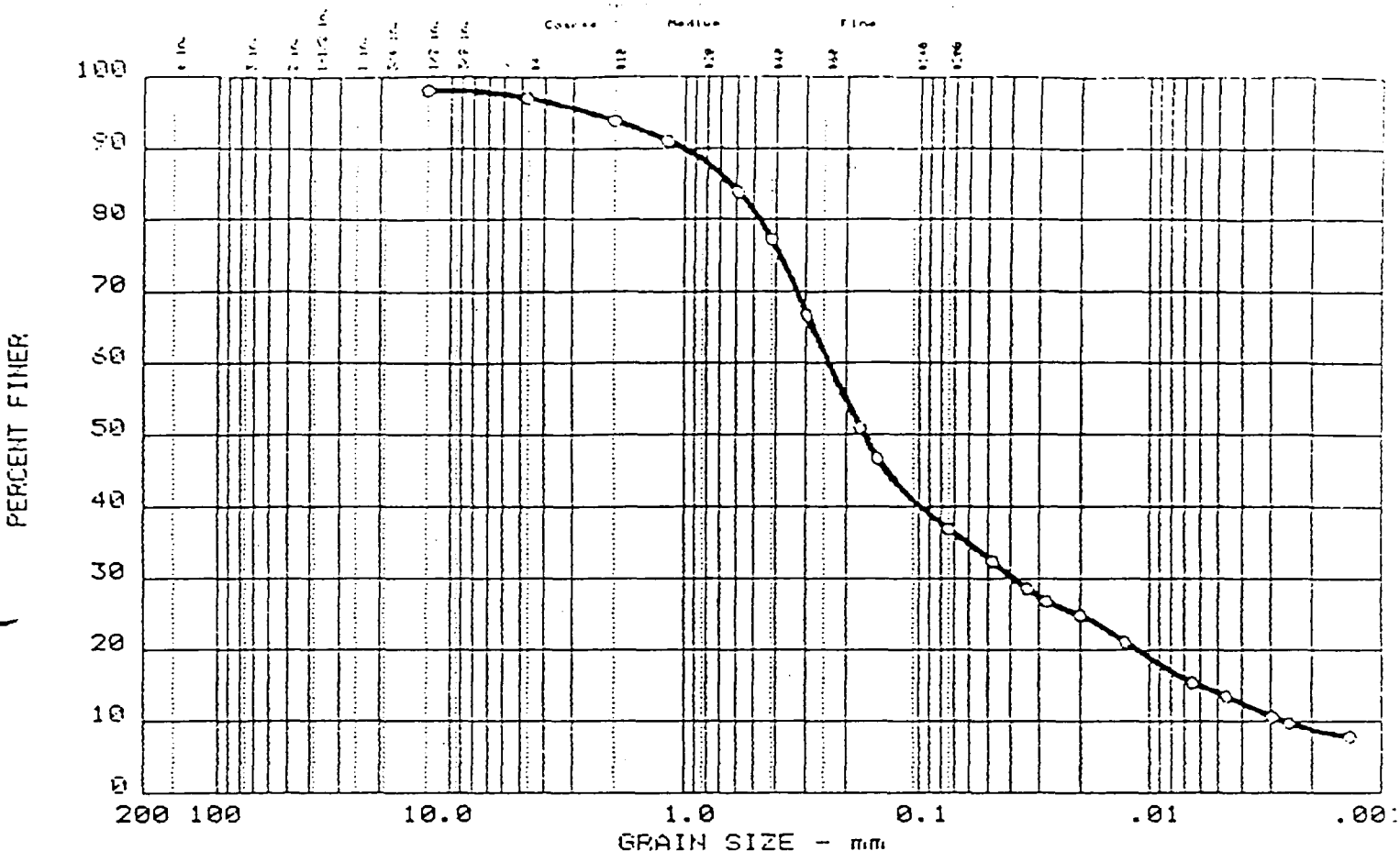
Date: 7/23/91

Remarks:
TESTED BY DWA/RWP
CHECKED BY DWA
APPROVED BY VJR

GRAIN SIZE DISTRIBUTION TEST REPORT
WARZYN, INC.

Sheet No.

GRAIN SIZE DISTRIBUTION TEST REPORT



Symbol	%+3"	% GRAVEL	% SAND	% SILT	% CLAY
O	0.0	2.9	60.1	23.0	13.9

	LL	PI	D_{85}	D_{60}	D_{50}	D_{30}	D_{15}	D_{10}	C_c	C_u
O	20	9	0.63	0.24	0.17	0.038	0.0060	0.0026	2.37	92.3

MATERIAL DESCRIPTION	USCS
O Brown Fine-Coarse SAND, Some Silt & Clay, Trace Gravel	SC

Project No.: 50422.00
Project:
O Sample: BORING: 3 SAMPLE: 6C @ 38.5-40.0 FT

Date: 07/14/89

GRAIN SIZE DISTRIBUTION TEST REPORT
WARZYN ENGINEERING INC.

Remarks:
TESTED BY: MML/DWA
ENTERED BY: MML
CHECKED BY:
APPROVED BY:

Sheet No.

May 6, 1988
99194

PARTICLE-SIZE ANALYSIS OF SOIL

ASTM D 422-63

Procedure to make dispersing agent and calibration:

1. Add 40 grams Sodium Hexametaphosphate to 1000 cc of De-aired Demineralized Water at 20°C. (160gm/4000cc)
2. Add 11.7 grams Sodium Bicarbonate to each 1000cc of agent (brings PH to 8.3) (35 gm/4000cc)
3. Allow to Stand for 24 Hours Before Using. Mix Thoroughly.
4. Mark Stock Solution with Date and Discard at 30 days.
5. Each Soil Sample Receives 125 ml of Stock Solution.
6. Add 125 ml of Stock Solution to a 1000 ml Sedimentation Cylinder and Fill to the 1000 ml mark with Demineralized Water at 20° C.
7. Record Correction Factor with a 152H Hydrometer. Record Temp. (should be 20°).

HYDROMETER CORRECTION

FLUID	SOLIDS ADDED	HYDROMETER READING GM/LITER (152 H Hydrometer)
Cold Tap Water	None	+1
Hot Tap Water	None	0
Hot Tap Water	Deflock Agent	+6
Cold Tap Water	Deflock Agent	+7
Distilled Water	Deflock Agent	+6

99194.00
DWA/mml/DWA
[mml-401-92]

APPENDIX B-17

DENSITY (WARZYN)

Designation: D 854 – 83

American Association State
Highway and Transportation Officials Standard
AASHTO No.: T 100

Standard Test Method for SPECIFIC GRAVITY OF SOILS[1]

This standard is issued under the fixed designation D 854; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers determination of the specific gravity of soils by means of a pycnometer. When the soil is composed of particles larger than the No. 4 (4.75-mm) sieve, the method outlined in Test Method C 127 shall be followed. When the soil is composed of particles both larger and smaller than the No. 4 sieve, the sample shall be separated on the No. 4 sieve and the appropriate test method used on each portion. The specific gravity value for the soil shall be the weighted average of the two values (Note 1). When the specific gravity value is to be used in calculations in connection with the hydrometer portion of Method D 422, it is intended that the specific gravity test be made on that portion of the soil which passes the No. 10 (2.00-mm) sieve.

NOTE 1—The weighted average specific gravity should be calculated using the following equation:

$$G_{avg} = \frac{1}{\frac{R_1}{100G_1} + \frac{P_1}{100G_2}}$$

where:

G_{avg} = weighted average specific gravity of soils composed of particles larger and smaller than the No. 4 (4.75-mm) sieve,
R_1 = percent of soil particles retained on the No. 4 sieve,
P_1 = percent of soil particles passing the No. 4 sieve,
G_1 = apparent specific gravity of soil particles retained on the No. 4 sieve as determined by Test Method C 127, and
G_2 = specific gravity of soil particles passing the No. 4 sieve as determined by this test method.

1.2 The values stated in acceptable metric units are to be regarded as the standard.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Applicable Documents

2.1 *ASTM Standards:*

C 127 Test Method for Specific Gravity and Absorption of Coarse Aggregate[2]
C 670 Practice for Preparing Precision Statements for Test Methods for Construction Materials[2]
D 422 Method for Particle-Size Analysis of Soils[3]
E 12 Definitions of Terms Relating to Density and Specific Gravity of Solids, Liquids, and Gases[4]

3. Definition

3.1 *specific gravity*—the ratio of the mass of a unit volume of a material at a stated temperature to the mass in air of the same volume of gas-free distilled water at a stated temperature (per Definitions E 12).

---

[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

Current edition approved Nov. 28, 1983. Published January 1984. Originally issued as D 854 – 45. Last previous edition D 854 – 58 (1979).

[2] *Annual Book of ASTM Standards*, Vol 04.02.
[3] *Annual Book of ASTM Standards*, Vol 04.08.
[4] *Annual Book of ASTM Standards*, Vol 15.05.

4. Significance and Use

4.1 The specific gravity of a soil is used in almost every equation expressing the phase relationship of air, water, and solids in a given volume of material.

4.2 The term "solid particles," as used in geotechnical engineering, is typically assumed to mean naturally occurring mineral particles that are not very soluble in water. Therefore, the specific gravity of materials containing extraneous matter (such as cement, lime, etc.), water-soluble matter (such as sodium chloride), and soils containing matter with a specific gravity of less than one, typically require special treatment or a qualified definition of specific gravity.

5. Apparatus

5.1 *Pycnometer*—Either a volumetric flask having a capacity of at least 100 mL or a stoppered bottle having a capacity of at least 50 mL (Note 2). The stopper shall be of the same material as the bottle, and of such size and shape that it can be easily inserted to a fixed depth in the neck of the bottle, and shall have a small hole through its center to permit the emission of air and surplus water.

NOTE 2—The use of either the volumetric flask or the stoppered bottle is a matter of individual preference, but in general, the flask should be used when a larger sample than can be used in the stoppered bottle is needed due to maximum grain size of the sample.

5.2 *Balance*—Either a balance sensitive to 0.01 g for use with the volumetric flask, or a balance sensitive to 0.001 g for use with the stoppered bottle.

6. Calibration of Pycnometer

6.1 The pycnometer shall be cleaned, dried, weighed, and the weight recorded. The pycnometer shall be filled with distilled water (Note 3) essentially at room temperature. The weight of the pycnometer and water, W_a, shall be determined and recorded. A thermometer shall be inserted in the water and its temperature T_i determined to the nearest whole degree.

NOTE 3—Kerosine is a better wetting agent than water for most soils and may be used in place of distilled water for oven-dried samples.

6.2 From the weight W_a determined at the observed temperature T_i a table of values of weights W_a shall be prepared for a series of temperatures that are likely to prevail when weights W_b are determined later (Note 4). These values of W_a shall be calculated as follows:

$$W_a \text{ (at } T_x\text{)} = (\text{density of water at } T_x/\text{density of water at } T_i) \times (W_a(\text{at } T_i) - W_f) + W_f$$

where:

W_a = weight of pycnometer and water, g,
W_f = weight of pycnometer, g,
T_i = observed temperature of water, °C, and
T_x = any other desired temperature, °C.

NOTE 4—This method provides a procedure that is most convenient for laboratories making many determinations with the same pycnometer. It is equally applicable to a single determination. Bringing the pycnometer and contents to some designated temperature when weights W_a and W_b are taken, requires considerable time. It is much more convenient to prepare a table of weights W_a for various temperatures likely to prevail when weights W_b are taken. It is important that weights W_a and W_b be based on water at the same temperature. Values for the relative density of water at temperatures from 18 to 30°C are given in Table 1.

7. Sampling

7.1 The soil to be used in specific gravity test may contain its natural moisture or be oven-dried. The weight of the test sample on an oven-dry basis shall be at least 25 g when the volumetric flask is to be used, and at least 10 g when the stoppered bottle is to be used.

7.2 *Samples Containing Natural Moisture*—When the sample contains its natural moisture, the weight of the soil, W_s, on an oven-dry basis shall be determined at the end of the test by evaporating the water in an oven maintained at 230 ±9°F (110 ±5°C) (Note 5). Samples of clay soils containing their natural moisture content shall be dispersed in distilled water before placing in the flask, using the dispersing equipment specified in Method D 422 (Note 6).

7.3 *Oven-Dried Samples*—When an oven-dried sample is to be used, the sample shall be dried for at least 12 h, or to constant weight, in an oven maintained at 230 ±9°F (110 ±5°C) (Note 5), cooled in a desiccator, and weighed upon removal from the desiccator. The sample shall then be soaked in distilled water for at least 12 h.

NOTE 5—Drying of certain soils at 110°C may bring about loss of moisture of composition or hydration, and in such cases drying shall be done, if desired, in reduced air pressure and at a lower temperature.

NOTE 6—The minimum volume of slurry that can be prepared by the dispersing equipment specified in Method D 422 is such that a 500-mL flask is needed as the pycnometer.

8. Procedure

8.1 Place the sample in the pycnometer, taking care not to lose any of the soil in case the weight of the sample has been determined. Add distilled water to fill the volumetric flask about three-fourths full or the stoppered bottle about half full.

8.2 Remove entrapped air by either of the following methods: (*1*) subject the contents to a partial vacuum (air pressure not exceeding 100 mm Hg) or (2) boil gently for at least 10 min while occasionally rolling the pycnometer to assist in the removal of the air. Subject the contents to reduced air pressure either by connecting the pycnometer directly to an aspirator or vacuum pump, or by use of a bell jar. Some soils boil violently when subjected to reduced air pressure. It will be necessary in those cases to reduce the air pressure at a slower rate or to use a larger flask. Cool samples that are heated to room temperature.

8.3 Fill the pycnometer with distilled water, clean the outside and dry with a clean, dry cloth. Determine the weight of the pycnometer and contents, W_b, and the temperature in degrees Celsius, T_x, of the contents as described in Section 6.

9. Calculation and Report

9.1 Calculate the specific gravity of the soil, based on water at a temperature T_x, as follows:

$$\text{Specific gravity, } T_x/T_x = W_o/[W_o + (W_a - W_b)]$$

where:

W_o = weight of sample of oven-dry soil, g,
W_a = weight of pycnometer filled with water at temperature T_x (Note 7), g,
W_b = weight of pycnometer filled with water and soil at temperature T_x, g, and
T_x = temperature of the contents of the pycnometer when weight W_b was determined, °C.

NOTE 7—This value shall be taken from the table of values of W_a, prepared in accordance with 6.2, for the temperature prevailing when weight W_b was taken.

9.2 Unless otherwise required, specific gravity values reported shall be based on water at 20°C. The value based on water at 20°C shall be calculated from the value based on water at the observed temperature T_x, as follows:

$$\text{Specific gravity, } T_x/20\text{ C} = K \times \text{specific gravity, } T_x/T_x$$

where:

K = a number found by dividing the relative density of water at temperature T_x by the relative density of water at 20°C. Values for a range of temperatures are given in Table 1.

9.3 When it is desired to report the specific gravity value based on water at 4°C, such a specific gravity value may be calculated by multiplying the specific gravity value at temperature T_x by the relative density of water at temperature T_x.

9.4 When any portion of the original sample of soil is eliminated in the preparation of the test sample, the portion on which the test has been made shall be reported.

10. Precision and Bias

10.1 Criteria for judging the acceptability of specific gravity test results obtained by this test method on material passing the No. 4 (4.75-mm) sieve are given as follows (Note 8):

Material and Type Index	Standard Deviation[A]	Acceptable Range of Two Results (percent of mean)[A]
Single-operator precision:		
Cohesive soils	0.021	0.06
Noncohesive soils	[B]	[B]
Multilaboratory precision:		
Cohesive soils	0.056	0.16
Noncohesive soils	[B]	[B]

[A] These numbers represent, respectively, the (1S) and (D2S) limits as described in Practice C 670.

[B] Criteria for assigning standard deviation values for noncohesive soils are not available at the present time.

NOTE 8—The figures given in Column 2 are the standard deviations that have been found to be appropriate for the materials described in Column 1. The figures given in Column 3 are the limits that should not be exceeded by the difference between the results of two properly conducted tests.

TABLE 1 Relative Density of Water and Conversion Factor K For Various Temperatures

Temperature, °C	Relative Density of Water	Correction Factor *K*
18	0.9986244	1.0004
19	0.9984347	1.0002
20	0.9982343	1.0000
21	0.9980233	0.9998
22	0.9978019	0.9996
23	0.9975702	0.9993
24	0.9973286	0.9991
25	0.9970770	0.9989
26	0.9968156	0.9986
27	0.9965451	0.9983
28	0.9962652	0.9980
29	0.9959761	0.9977
30	0.9956780	0.9974

SPECIFIC GRAVITY OF SOIL SOLIDS (G_s)

Project _____ Job No. _____

Location of Project _____ Boring No. _____ Sample No. _____

Description of Soil _____ Depth of Sample _____

Tested By _____ Date of Testing _____

Test no.				
Vol. of flask at 20°C				
Method of air removal[a]				
Wt. flask + water + soil = W_{bws}				
Temperature, °C				
Wt. flask + water[b] = W_{bw}				
Evap. dish no.				
Wt. evap. dish + dry soil				
Wt. of evap. dish				
Wt. of dry soil = W_s				
$W_w = W_s + W_{bw} - W_{bws}$				
$G_s = \alpha W_s / W_w$				

[a]Indicate vacuum or aspirator for air removal.

[b]W_{bw} is the weight of the flask filled with water with the same quantity of dispersing agent as added to the soil–water mixture and at the same temperature.

Remarks _____

_____

Average specific gravity of soil solids (G_s) = _____

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